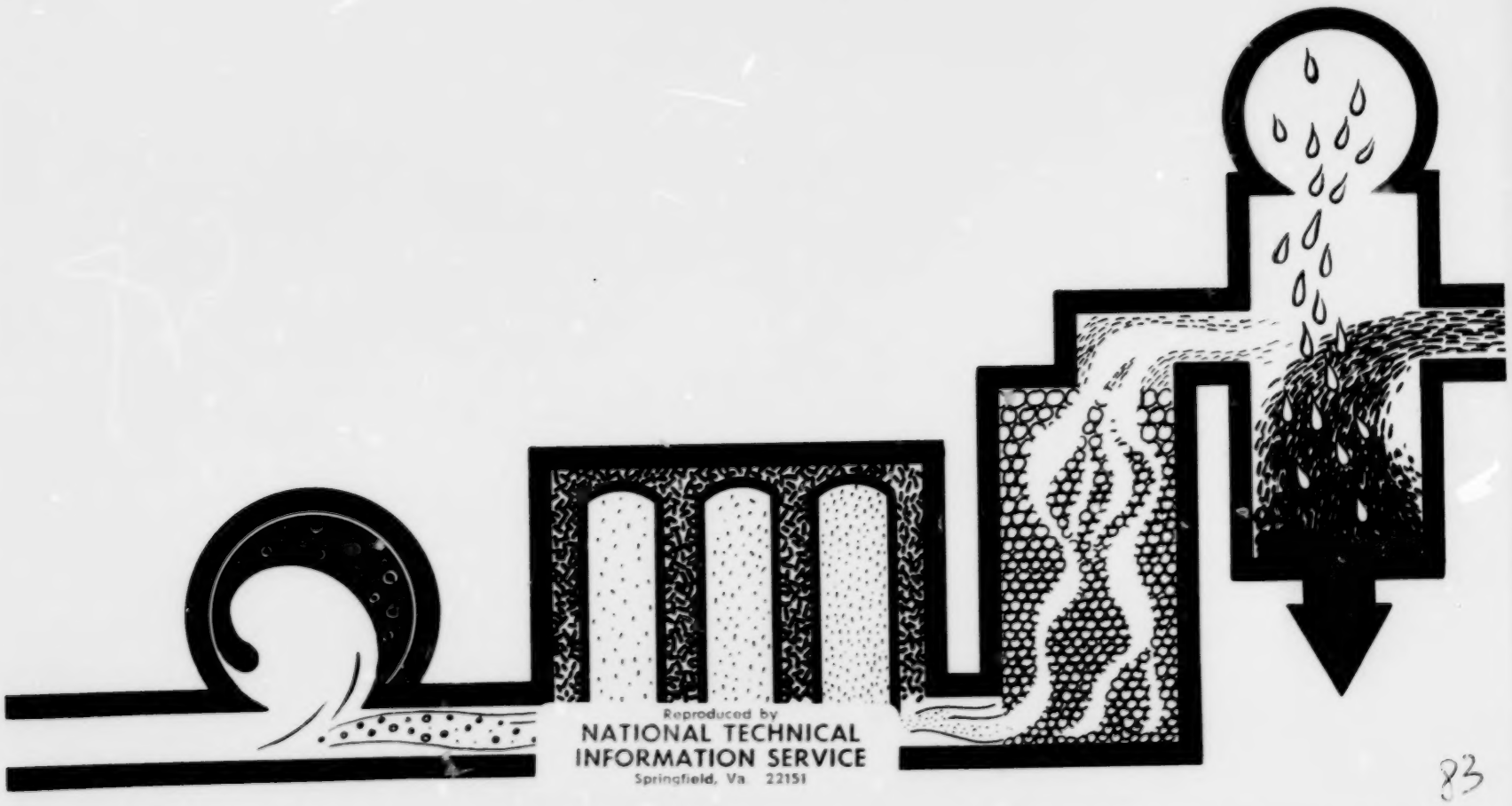
PB 197 671

WATER POLLUTION CONTROL RESEARCH SERIES • ORD- 17030EOH01/70

W71-04671

APPLICATION OF HYPERFILTRATION TO TREATMENT OF MUNICIPAL SEWAGE EFFLUENTS



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

83

U.S. DEPARTMENT OF THE INTERIOR • FEDERAL WATER QUALITY ADMINISTRATION

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development, and demonstration activities of the Federal Water Quality Administration, Department of the Interior, through in-house research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Water Pollution Control Research Reports will be distributed to requesters as supplies permit. Requests should be sent to the Planning and Resources Office, Office of Research and Development, Federal Water Quality Administration, Department of the Interior, Washington, D. C. 20242.

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 70 cents

1 Accession Number: W71-04671

2 Subject Field & Group: 05D, 03A

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

5 Organization

Oak Ridge National Laboratory, Oak Ridge, Tennessee, Water Research Program,

6 Title

APPLICATION OF HYPERFILTRATION TO TREATMENT OF MUNICIPAL SEWAGE EFFLUENTS,

10 Author(s)

Kraus, Kurt A

16 Project Designation

FWQA Program #17030 EOH

21 Note

I 67.13/4:17030EOH01/70
Copy available from ~~GPO Sup Doc~~ as , $0.70; microfiche ~~from NTIS as PB~~ 197671, $0.95.

22 Citation

Water Pollution Control Research Series 17030 EOH 01/70, January 1970. 71p,

23 Descriptors (Starred First)

Waste water treatment, *Filtration, *Membranes, Membrane processes, Effluents, Municipal wastes, Sewage effluents, *Sewage treatment, *Electrolytes, Ion exchange,

25 Identifiers (Starred First)

*Hyperfiltration, Membrane additives,

27 Abstract

A large number of membranes dynamically formed from polyelectrolytes on fine-grained (ca. 0.5 μ) supports or filters were tested for application in hyperfiltration of effluents from the primary and secondary stages of a municipal sewage treatment plant. Since results with primary effluents were not significantly different from those with secondary, most of the later studies were limited to primary effluents.

The dynamic membranes were principally examined for salt rejection, organic rejection, flux, and flux decline with time. Cation-exchange membranes formed from anionic polyelectrolytes were generally superior to anion exchange membranes from polycations. Membranes formed from (unidentified) sewage constituents, while rejecting salts and organic materials, seemed inferior to separately formed dynamic cation-exchange-active membranes.

In earlier studies, membrane additives were continuously supplied to the feeds. In later runs, which extended to several weeks' operation at the sewage plant, such continuous addition did not seem required, at least for some of the more promising membrane additives tested, such as those formed from homogenized Dowex-50, homogenized Sephadex, and for a dual-layer membrane composed of hydrous zirconium oxide and polyacrylic acid. With these membranes, upward of 50% salt rejection was frequently found, together with higher alkaline earth and organic rejections at initial fluxes of 100 gfd and higher. Salt rejection in excess of 50% at fluxes in excess of 50 gfd were found in 60% of the cases after 20 hours operation. At high circulation velocities (larger than 20 ft/sec), flux decline was usually modest, and fluxes in excess of 50 gfd were often observed after two weeks' operation.

Abstractor

WR:102
WRSIC

I CENTER

70-389-930

APPLICATION OF HYPERFILTRATION TO TREATMENT OF MUNICIPAL SEWAGE EFFLUENTS

by

Water Research Program
Kurt A. Kraus, Director

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

for the

FEDERAL WATER QUALITY ADMINISTRATION

DEPARTMENT OF THE INTERIOR

Program #17030 EOH
Contract #14-12-423
FWQA Project Officer, W. A. Schwartz
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
January, 1970

FWQA Review Notice

This report has been reviewed by the Federal Water Quality Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Quality Administration, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A large number of membranes dynamically formed from polyelectrolytes on fine-grained (ca. 0.5 μ) supports or filters were tested for application in hyperfiltration of effluents from the primary and secondary stages of a municipal sewage treatment plant. Since results with primary effluents were not significantly different from those with secondary, most of the later studies were limited to primary effluents.

The dynamic membranes were principally examined for salt rejection, organic rejection, flux, and flux decline with time. Cation-exchange membranes formed from anionic polyelectrolytes were generally superior to anion exchange membranes from polycations. Membranes formed from (unidentified) sewage constituents, while rejecting salts and organic materials, seemed inferior to separately formed dynamic cation-exchange-active membranes.

In the earlier studies, membrane additives were continuously supplied to the feeds. In later runs, which extended to several weeks operation at the sewage plant, such continuous addition did not seem required, at least for some of the more promising membrane additives tested, such as those formed from homogenized Dowex-50, homogenized Sephadex, and for a dual-layer membrane composed of hydrous zirconium oxide and polyacrylic acid. With these membranes, upward of 50% salt rejection was frequently found, together with higher alkaline earth and organic rejections at initial fluxes of 100 gfd and higher. Salt rejection in excess of 50% at fluxes in excess of 50 gfd were found in 60% of the cases after 20 hours operation. At high circulation velocities (larger than 20 ft/sec), flux decline was usually modest, and fluxes in excess of 50 gfd were often observed after two weeks' operation.

This report was submitted in fulfillment of Contract No. 14-12-423, Program No. 17030 EOH, between the Federal Water Quality Administration and Oak Ridge National Laboratory.

CONTENTS

Page

ABSTRACT

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION 1

SUMMARY OF RESULTS 2

Self-rejecting Systems 8
Systems with Continuous Addition of Additives 13
Systems without Additives and with Preformed Membranes . . . 13

CONCLUSIONS AND RECOMMENDATIONS 16

EQUIPMENT AND EXPERIMENTAL PROCEDURES 17

Bench-type Hyperfiltration Loop 18
Mobile Hyperfiltration Loop 18
Stationary 100-gpm Hyperfiltration Loop 20
Test Sections. 20
Experimental Procedures 23
Additives 23
Analyses 24

RESULTS 24

Preliminary Survey 24
Anion-Exchange vs Cation-Exchange Membranes 24
Effect of Pressure 27
Preformed vs Nonpreformed Membranes 27
Pore Size and Support Effects 27
Organic Carbon Rejections 30
Summary 30

Long-Term Runs with Secondary Effluent 31
Treatment of Secondary Effluent with Homogenized Low Cross-Linked Ion-Exchange Membranes 31
Comparison of Hyperfiltration of Primary and Secondary Effluents by a Dowex-50X 0.25 Membrane. . . . 33
Two-Stage Treatment 35

Long-Term Runs with Primary Effluent 36
Runs 58, 59, 60 36
Run 61. 39
Run 62. 39
Run 66. 43
Run 67. 45
Run 68. 48
Run 69. 48
Run 70. 50
Run 71. 53
Run 72. 55

DISCUSSION. 59

Velocity Effects 59
Flux Decline 64
Rejection-Flux Relation 68

LIST OF FIGURES

		Page
Fig. 1.	Interior View of the Mobile Hyperfiltration System . .	19
Fig. 2.	Schematic Flow Diagram of Typical Hyperfiltration Loop	21
Fig. 3.	Hyperfiltration Test Section with Transparent Pressure Jacket	22
Fig. 4.	Hyperfiltration of Effluent from Secondary Sewage Treatement with Dynamically Formed Poly(maleic Acid) Membrane	25
Fig. 5.	Hyperfiltration of Effluent from Secondary Treatment of Oak Ridge Sewage	32
Fig. 6.	Run 48: Hyperfiltration of Sewage Effluents (Dowex-50 X 0.25 membrane on 0.45-μ support, 75°F) . .	34
Fig. 7.	Run 62: Hyperfiltration of Primary Sewage Effluents with 0.01 M NaCl Spike (Dowex-50 X 0.5 membrane on 0.45-μ support, 100°F).	41
Fig. 8.	Hyperfiltration of Primary Sewage Effluent, Behavior of Flux Following Various Events (Numbers with each Curve are Slopes of Curves)(Run 62: Dowex-50 X 0.5 membrane on 0.45-μ support, 1000 psi, 100°F)	42
Fig. 9.	Hyperfiltration of Primary Sewage Effluent (Run 67: Dowex-50 X 0.5 membrane on 0.45-μ Acropor support, 1000 psi, 98°F).	47
Fig. 10.	Hyperfiltration Properties of a Polyacrylate Membrane with Primary Effluent Feed	49
Fig. 11.	Run 70: Hyperfiltration of Primary Sewage Effluents with 0.01 M NaCl Spike (Feed Pressure 1000 psig, feed velocity, 30.5 fps)	52
Fig. 12.	Hyperfiltration of Effluent from Primary Treatment of Sewage with Dynamically Formed Membranes	54
Fig. 13.	Comparison of Hyperfiltration of Primary Sewage Effluent by Membrane Formed from Feed Constituents with Sephadex CM C-50 Membranes (Run 72: 1000 psig, 30 ft/sec) . .	58
Fig. 14.	Effect of Axial Velocity on Flux and Rejection of Preformed Dowex-50 X 0.25 Membrane after 20 Hours of Operation with Primary Sewage Feed (1000 psi, 0.45-μ Acropor support)	60

LIST OF FIGURES (Continued)

Page

Fig. 15. Effect of Axial Velocity on Flux and Rejection of Preformed Dowex-50 X 0.25 Membrane after 100 Hours of Operation with Primary Sewage Feed (1000 psi, 0.45-μ Acropor support) 61

Fig. 16. Effect of Axial Velocity on Flux and Rejection of Preformed Dowex-50 X 0.25 Membrane after 200 Hours of Operation with Primary Sewage Feed (1000 psi, 0.45-μ Acropor support) 62

Fig. 17. Effect of Axial Velocity on Flux and Rejection of Preformed Dowex-50 X 0.25 Membrane after 400 Hours of Operation with Primary Sewage Feed (1000 psi, 0.45-μ Acropor support) 63

Fig. 18. Comparison of Different Membranes and Primary Sewage Alone with Performance of Dowex-50 X 0.25 Membrane (Solid Curves Outline Scatter Band of Dowex-50 from Fig. 14) after 20 Hours Operation with Primary Sewage (1000 psi, 0.45-μ Acropor support). 65

Fig. 19. Comparison of Different Membranes and Primary Sewage Alone with Performance of Dowex-50 X 0.25 Membrane (Solid Curves Outline Scatter Band of Dowex-50 from Fig. 15) after 100 Hours Operation with Primary Sewage (1000 psi, 0.45-μ Acropor support) 66

Fig. 20. Effect of Time on Flux using Primary Sewage Feed and Preformed Dowex-50 X 0.25 Membrane at an Axial Velocity of 20 ft/sec. (1000 psi, 0.45-μ Acropor support, points and limits on curves are best fit, maximum and minimum values from Figs. 14-17). 67

Fig. 21. Flux-Rejection Results after 20 Hours Exposure to Primary Sewage Effluent at 1000 psi Operating Pressure. [(a) S = Sephadex; (b) P = Primary sewage with no additives] 69

LIST OF TABLES

		Page
Table 1.	Additives, Loops, and Type of Sewage Tested for Hyperfiltration of Oak Ridge Sewage Effluents with Dynamically Formed Membranes	4
Table 2.	Characteristics and Source of Additives Tested for Hyperfiltration of Oak Ridge Sewage Effluents with Dynamically Formed Membranes	5
Table 3.	Porous Materials Used as Supports for Dynamic Membranes for Hyperfiltration of Oak Ridge Sewage Effluents	9
Table 4.	Summary of Trailer Loop Runs at Sewage Plant	10
Table 5.	Summary of Membrane Performance and Operating Conditions at an Operating Time of 20 Hours with Secondary Sewage in the Stainless Steel Loop at Y-12 (C-Loop)	12
Table 6.	Typical Effects of Sewage Effluents on Hyperfiltration by Dynamically Formed Membranes (0.01 M NaCl in Secondary Effluent; Bench Loop, Millipore Supports)	26
Table 7.	Comparison of Hyperfiltration Properties of Preformed Membranes and of Membranes Formed of Polyelectrolytes Added to Sewage Feeds (Effluent from Secondary Treatment of Municipal Sewage; 0.025 μ Millipore Supports; Bench Loop; 0.01 M NaCl)	28
Table 8.	Comparison of Hyperfiltration of Secondary Sewage Effluent by Membranes on Millipore Supports of Different Pore Sizes	29
Table 9.	Materials and Operating Conditions for Runs of Over 100 Hours with Primary Sewage	37
Table 10.	Performance of Dowex-50 on 0.45μ Acropor (A,C) and 0.45μ Nuclepore (B) with Unspiked Secondary Sewage after 8 Hours Operation (Run 58)	38
Table 11.	Performance of Dowex-50 on 0.45μ Acropor with Unspiked Primary Sewage (Cumulative Running Time 64 Hours) (Run 59)	38
Table 12.	Performance of Sewage Membrane on Hose and D50 Membrane (Unspiked Primary Sewage 8 Hours after Startup; Cumulative Running Time 106 Hours for D50)(Run 60) . .	38
Table 13.	Membrane Performance after 22 Hours Operation with Unspiked Primary Sewage (Run 61)	40

LIST OF TABLES (Continued)

		Page
Table 14.	Effect of First NaOH Wash at 373 Hours	43
Table 15.	Performance of D-50 X 0.5 Membranes on 0.45μ Primary Sewage (Run 62)	44
Table 16.	The Effect of Pressure on Performance of D-50 X 0.5 Membranes on Acropor with Primary Sewage (Run 66, 85 Hours)	45
Table 17.	Effect of Circulation Velocity in Short-Term Traverse with Dowex-50 X 0.5 Membrane (~20 Minutes at Each Velocity)	45
Table 18.	Membrane Performance Before and After Na_2CO_3 Wash (Run 67)	46
Table 19.	Membrane Forming Conditions and Performance for Test Sections of Run 70	51
Table 20.	Test Section Materials and Performance at End of Membrane Formation for Run 71 Membranes	53
Table 21.	Run 71. Effect of Pressure on Flux and Chloride Rejection	56
Table 22.	Run 71. Summary of Organic Carbon Rejection Results .	57
Table 23.	Test Section Materials and Performance at End of Formation for Run 72 Membranes (Feed: 0.01 M NaCl) . .	57

APPLICATION OF HYPERFILTRATION TO TREATMENT OF MUNICIPAL SEWAGE EFFLUENTS

INTRODUCTION

From 1963, when initial studies (1) were begun using municipal sewage effluents as feeds, it has been recognized that hyperfiltration (reverse osmosis) held promise as a process yielding water suitable for reuse. These experiments (1) with cellulose acetate membranes demonstrated that water recoveries of 80 to 90% were possible, that product water contained less than 80 mg/ℓ total dissolved solids, less than 0.3 mg/ℓ detergents and less than 10 mg/ℓ oxygen-demanding substances when the sewage effluent feed contained 600 to 800 mg/liter total dissolved solids, 5 to 10 mg/ℓ detergents and 80 to 120 mg/ℓ chemical oxygen demanding substances. These tests also showed that there was appreciable flux decline with time even when the initial flux was 5 to 10 gal/ft^2·day (gfd). Other tests (2) showed that only modest flux declines (~20% in 1600 hours) occurred when the initial flux was ~2 gfd but that substantial flux declines occurred (with a different membrane) when the initial flux was ~10 gfd.

Subsequent studies (3-6) of hyperfiltration of sewage effluent showed that, with cellulose acetate membranes tailored for brackish water desalination, rejection of inorganics (except nitrogen compounds) can be 90 to 95% or better. However, rejection of ammonia, phenols and low molecular weight organics is not as satisfactory. Although the flux decline problem has not been overcome, recent studies (6) indicate that it may be possible to clean membranes in-situ using chemical agents such as sodium hydrosulfite, acetic acid or laundry presoak formulations containing enzymes.

In work carried out at the Oak Ridge National Laboratory under Office of Saline Water Sponsorship, it was discovered that salt-rejecting membranes can be formed by passing a pressurized dilute dispersion of a suitable additive over a porous support having pore diameters in the micron range (7). A wide variety of additives has been found to form salt-rejecting membranes in this manner, apparently by formation of an additive layer at the membrane-feed interface. Very interesting membranes are formed of poly-electrolytes for which — unlike neutral membranes such as cellulose acetate — an ion-exclusion mechanism is involved in salt filtration. Transmission rates through dynamic membranes are sometimes very high, up to several hundred gallons per square foot per day, but salt rejections are characteristically lower than by cellulose acetate, and are concentration dependent, rejection increasing with decreasing salt concentration of the feed.

It is not always necessary to put additives into feed solutions; substances already present may form membranes dynamically. For example,

with wash liquors from the sulfite pulping process, membranes which filtered most of the lignosulfonates and a modest fraction of salt were formed from the feed solutions (8). Similarly, constituents of primary-treated municipal sewage also formed membranes from feed constituents; these membranes rejected typically a quarter to a third of dissolved solids, and 80 to 90% of chemical oxygen demand, at fluxes of 50 gfd (450 psig) over a period of several days (9).

The advantage of high fluxes, so far usually obtained with dynamically formed membranes, may be overbalanced by lower rejections in applications involving only desalination. This, however, is less likely to be the case in sewage treatment. Concentrations of dissolved salts are usually lower than those of the usual candidates for desalination, even the low-salinity natural (brackish) waters. Further, rejection requirements are not as high. Typically concentration is increased by a few hundred ppm in the cycle of municipal use, and only salt added needs to be removed to reduce salt concentration to that of the municipal water supply for reuse or for discharge to surface water. Fifty percent rejection, for example, would allow recovery of a useful fraction in many cases.

A program sponsored by the Federal Water Quality Administration on the application of dynamically formed membranes to the treatment of municipal sewage effluents was initiated at Oak Ridge National Laboratory in July 1968. The principal purpose of the work was to establish technical feasibility of a tertiary municipal sewage effluent treatment process based on hyperfiltration with dynamically formed membranes for removal or organics and salts. Some exploratory work with primary sewage effluents was also authorized. In view of the encouraging results, emphasis during the latter part of the contract period was shifted to emphasize the treatment of primary sewage effluents.

SUMMARY OF RESULTS

In the proposal submitted to FWQA in April, 1968, we suggested work with municipal sewage effluents on salt and organic rejecting properties of membranes dynamically formed from feed constituents; on membranes dynamically formed from additives; on identifying suitable support structures and on the effect of important variables and of the hydrodynamic conditions. In the request for extension, May, 1969, we further suggested more detailed tests with a number of the more promising additives; longer term tests at the Oak Ridge Sewage plant; establishment of lower concentration limits required of additives; determination of effect of pressure and circulation velocity on performance.

Most of the early work was carried out with secondary (activated sludge) effluent from the Oak Ridge sewage plant as feed. The more recent studies were with effluent from the primary stage. Since the sewage had a very low dissolved solids level ($\sim$ 100 mg/liter) in most

cases the solutions were "spiked" to ca 0.008 M NaCl to facilitate analyses. This also served to simulate a dissolved solids level more typical of secondary effluents generally, as well as the effect of concentrating the feed. (For most of the membranes tested, salt rejection decreases with concentration.) Judgment regarding filtration performance in the early phases of the work was primarily based on chloride analyses and flux measurements. These were later supplemented with organic and inorganic carbon, alkaline earth and phosphate analyses, and turbidity measurements.

During the early work, principal emphasis was on screening additives and on establishing conditions suitable for forming dynamic membranes with which salt filtration of sewage could be achieved. The duration of the runs was from a few days to several weeks. The shorter runs were largely with the bench loop where the objective was to determine if the additive had any promise. Most of the longer runs were carried out during the last few months at the sewage plant with membranes prepared in a titanium loop and then transported to the plant.

A list of additives which were checked is given in Table 1. Additional details are given in Table 2 which also gives identification numbers used in later figures. The substances tested included negatively-charged synthetic polyelectrolytes such as polystyrene sulfonate and polyacrylic acid, positively charged polyelectrolytes such as polyvinyl amine and polyvinyl pyridine, polyelectrolytes derived from natural products such as sulfonated starches and carboxymethyl cellulose, industrial wastes such as pulp mill wastes, natural products such as humic acid and Leonardite (a highly oxidized lignite), and ground or homogenized low cross-linked ion exchange resins. Comparisons were carried out with membranes formed from unidentified constituents of the sewage.

Three different techniques were used for testing the "additives". In some cases, the materials were added to sewage and a membrane prepared by passing the mixture under pressure over porous support structures; the run was then continued by keeping varying amounts of this additive in the sewage. In other cases, the membrane was "preformed" by passing tap water containing the additive over the porous body until satisfactory performance was observed; sewage containing the same additive was then passed over the preformed membrane. In most of the later experiments, membranes were preformed and the sewage being processed did not contain further additives.

Most of the early work was carried out with a bench-type loop ("B") with small pressure cells containing flat circular membranes with ca 1.5 cm^2 area, Table 1. The table also lists, for completeness, later experiments carried out with a stationary stainless steel ("S") loop located at the Y-12 laboratory, a stationary titanium ("Ti") loop located at ORNL (X-10), and a mobile ("M") loop built in a trailer (not with FWQA funds) and located at the Oak Ridge East Sewage Plant.

TABLE 1

ADDITIVES, LOOPS, AND TYPE OF SEWAGE TESTED FOR HYPERFILTRATION OF OAK RIDGE SEWAGE EFFLUENTS WITH DYNAMICALLY FORMED MEMBRANES

	Membrane Type[a]	Loops Used	
		Secondary[b]	Primary[b]
Acrylamide-acrylate copolymer	C	B	
Amberlite IRC 50	C	B S	
Carboxymethyl cellulose	C	B S	
Dowex-1 (homogenized)	A	Ti	Ti
Dowex-50 (homogenized)	C	B S Ti M	Ti M
Humic acid	C	B S	
Hydrous oxides with polyacrylic acid	C		M
Leonardite (an oxidized lignite)	C	S	
Polyacrylic acid	C	B S	M
Polyacrylic acid (+ carbon)	C	S	
Polyacrylic acid (+ carbon + Leonardite)	C	S	
Polyacrylic acid + Fe(III)	C		M
Polyethylene imine	A	B	
Polymaleic acid	C	B	
Polystyrene sulfonate	C	B	
Polyvinyl amine	A	B	
Polyvinyl benzyl trimethyl ammonium chloride	A	B	
Polyvinyl sulfonate	C	B	
Poly 2-vinyl pyridine	A	B	
Poly 4-vinyl pyridinium butyl salt	A	B	
Pulp mill wastes	C	B S	
Sephadex	C		M
Sewage constituents	C(?)	B S	S[c] M
Sulfonated Starch	C	B S	

[a] C - Cation-exchange active; A - Anion-exchange active.

[b] Symbols designating loops used: B - bench loop
S - stationary stainless steel loop
M - mobile loop at sewage plant
Ti - stationary titanium loop

[c] Work published previously.

TABLE 2

CHARACTERISTICS AND SOURCE OF ADDITIVES TESTED FOR HYPERFILTRATION OF OAK RIDGE SEWAGE EFFLUENTS WITH DYNAMICALLY FORMED MEMBRANES

Number	Polyelectrolyte	Source	Notes
None	No additive; membrane from sewage feed constituents.		
Polyanionic(cation-exchange membranes)			
1	Poly(maleic anhydride)	Dow[a]	Hydrolyzes readily to poly(maleic acid)
2	Carboxymethyl cellulose, 7H	Hercules	Degree of polymerization, about 1000, ~0.7 substitution per hexose unit
3	Poly(acrylic acid) (PAA)	Borden	Most bench, stationary loop runs
		Rohm & Haas[b]	Acrysol A-5, MW about five times that of Borden material. Most mobile loop experiments
4	Poly(acrylic acid [1/3] co-acrylamide [2/3])	Dow[a]	MW ~3,000,000
5	Poly(vinyl sulfonate)	ORNL[c]	Two prep., MW ~35,000 and ~65,000; no clear difference between membrane properties
6	Poly(styrene sulfonate)	Dow[a]	
7	Starch Sulfate	National Starch & Chemical[d]	~1.5 sulfates/hexose
8	Sephadex CM-C-25 (homogenized)	Pharmacia	Carboxymethyl substituted dextran ion-exchanger, ~4.5 meq/g capacity
9	Humic acid	ORNL	See Experimental
10	Leonardite	Bureau of Mines[g] Knife River Coal Mining Company[h]	See Experimental

TABLE 2 (Continued)

Number	Polyelectrolyte	Source	Notes
11	Pulp Mill Waste		See Experimental
12	Amberlite IRC-50 (homogenized) plus PAA	Rohm & Haas	IRC-50 is a solid poly(methacrylate) cation-exchanger
13	Homogenized Dowex-50 X 0.25	Dow[a]	Poly(styrene sulfonate), cross linked with 0.25% divinyl benzene
14	Homogenized Dowex-50 X 0.5	Dow[a]	Poly(styrene sulfonate), cross linked with 0.5% divinyl benzene
15	Homogenized Dowex-50 X 1	Dow[a]	Poly(styrene sulfonate), cross linked with 1% divinyl benzene
16	PAA plus AquaNuchar A	Carbon: W. Va. Pulp & Paper	PAA = poly (acrylic acid)
17	PAA plus AquaNuchar A plus Leonardite		
18	PAA stabilized with hydrous Fe (III) oxide	Rohm & Haas (PAA)	
Polycationic (Anion-exchange membranes)			
22	Poly(vinyl amine)	ORNL[c]	
23	Poly(2-vinyl pyridine)	Ionac[e]	MW ~200,000
24	Poly(4-vinyl pyridinium butyl bromide) 80% quarternized	ORNL[c,f]	
25	Poly(vinyl benzyl trimethyl ammonium chloride)	Dow[a]	MW ~100,000
26	Polyethylenimine	Dow[a]	MW ~50,000 - 1,000,000
27	Dowex-1 X 0.25 (homogenized)	Dow[a]	Poly(vinyl benzyl trimethyl ammonium chloride), cross linked with 0.25% divinyl benzene

TABLE 2 (Continued)

---

[a]We thank R. M. Wheaton and R. E. Anderson and Dow Chemical Company for supplying us with these materials.

[b]We thank G. D. Button and the Rohm & Haas Corporation for supplying us these materials.

[c]We are indebted to W. H. Baldwin and C. E. Higgins for these preparations.

[d]We thank M. W. Rutenberg of National Starch and Chemical Corp. for this material.

[e]We thank C. Calmon and Ionac Chemical Company (Ritter-Pfaudler) for samples of poly(vinyl pyridine).

[f]We thank R. M. Fuoss, Yale University, for a sample of poly(4-vinyl pyridine).

[g]We thank D. J. Nelson of the ORNL Ecological Sciences Division for a sample of humic acid.

[h]We thank J. L. Elder, Grand Forks, N.D., Coal Research Laboratory, U.S. Bureau of Mines for a sample of Leonardite.

Porous support structures used included porous stainless steel tubes and plates, tubular ceramic filters, various grades of Millipore and Gelman (Acropor) filters, and woven fire hose jackets precoated in situ with filter-aids. A list of these with additional information is given in Table 3.

While we expected better rejection and lower fluxes with fine-grained supports and poorer rejection and higher fluxes with coarser grained supports including coated hoses, we found relatively little difference in rejection between the two types of supports. Where successfully tested the hoses usually showed very high initial fluxes (up to several hundred gfd). In general, where simultaneous comparison between various support structures was made, dramatic differences in fluxes were observed; frequently better rejection occurred at the higher flux.

Selection and identification of suitable (economical) support structures remains one of the principal unresolved questions. Although much of the most recent work was carried out with porous supports wrapped with filters such as Acropor or Millipore, we believe that woven hoses remain an attractive possibility. There is, of course, continuing need to explore other economical supports.

We have had some operating difficulties with hoses which we attribute to the particular hose available, rather than to flaws in the concept. Thus, we found that the hose tended to spring "leaks" at high pressures, presumably because of fiber separation when the pressure is on the inside of the hose. This difficulty was temporarily remedied by placing a tight-fitting metal sleeve with drill holes over the hose. We believe that with proper selection of weaves this difficulty could be remedied. We have also found that some additives are more difficult to deposit on precoated hoses than others. While excellent results could be obtained reproducibly with polyacrylic acid on hoses, the very promising homogenized low cross-linked ion exchangers have not yet yielded a satisfactory membrane on this support.

Table 4 is a summary of materials, operating conditions, and membrane performance at various times during a run for all runs completed in the mobile loop located at the Oak Ridge East Sewage Plant. A similar summary for sewage runs in the stationary, 100 gpm stainless steel loop is shown in Table 5.

Self-rejecting Systems (Systems with no additives)

We have confirmed at the Oak Ridge Sewage Plant that primary sewage effluents can form membranes which typically filter 35% of the salt and upward of 70% of the organic carbon at fluxes between 50-100 gfd at 750 psi at an axial velocity of 25 ft/sec. These results are similar to those which we published earlier (9) for primary effluents from the Knoxville Third Creek Plant, although some of the results obtained seem

TABLE 3

POROUS MATERIALS USED AS SUPPORTS FOR DYNAMIC MEMBRANES FOR HYPERFILTRATION OF OAK RIDGE SEWAGE EFFLUENTS

Letter	Material	Manufacturer or Supplier & Trade Designation	Nominal Pore Size Microns
None	Cellulose, mixed esters	Millipore VF	0.025
a	Cellulose, mixed esters	Millipore VC	0.1
b	Cellulose, mixed esters	Millipore GS	0.22
c	Cellulose, mixed esters	Millipore PH	0.3
d	Cellulose, mixed esters	Millipore HA	0.45
e	Poly(vinyl chloride co-acrylonitrile), nylon fabric reinforcement	Gelman Acropor AN 450	0.45
f	Stainless steel plates	Huyck Metals Co.	5
g	Ceramic	Selas 03	0.9*
h	Polyester or cotton, fire hose jackets	Fabric Fire Hose Co. Lewis Products Co.	

*Measured value (Ref. 8).

TABLE 4

SUMMARY OF TRAILER LOOP RUNS AT SEWAGE PLANT

Run No.	Duration Hrs.	Pressure psi	Velocity fps	Support[a]	Membrane[b]	20 Hours		100 Hours		200 Hours		400 Hours	
						R_{obs}[c]	J gfd	R_{obs}	J gfd	R_{obs}	J gfd	R_{obs}	J gfd
57*	18	500	44	0.45μ A	D50	48	294						
58*	11	1000	45	0.45μ A	D50	NA	NA						
	18		45	0.5 μ N	D50	34	64						
	54		45	0.45μ A	D50	53	149						
59	33	1000	44	0.45μ A	PAA	54	78						
	33		44	0.45μ A	D50[1]	65	71						
60	96	750	25	Hose	Primary	29	99	32	40				
	141		44	0.45μ A	D50[2]	55	110	37	76				
61	128	1000	44	0.45μ A	D50	67	127	37	31				
	3		44	0.45μ A	D50								
	128		44	0.025μ M	PAA	65	11	98.5	5				
62	546	1000	44	0.45μ A	D50	58	179	64	105	65	62	54	92
	546		31	0.45μ A	D50	60	128	63	103	64	52	51	105
	546		18	0.45μ A	D50	63	84	64	59	60	42	60	33
66	108	1000	44	0.45μ A	D50	72	110	70	93				
	61		31	0.45μ A	D50	73	75						
	108		18	0.45μ A	D50	67	68	66	50				
	61		6.8	0.45μ A	D50	72	25						
67	394	1000	44	0.45μ A	D50	41	185	46	122	58	54	35	42
	394		31	0.45μ A	D50	44	170	50	108	61	51	NA	NA
	394		18	0.45μ A	D50	62	68	65	45	71	24	67	17
	174		13	0.45μ A	D50	67	60	63	29	(70)	(15)		
68	138	1000	44	0.45μ A	PAA+$FeCl_3$	43	95	49	53				
	138		18	0.45μ A	D50[3]	62	16	61	5				

TABLE 4 (Continued)

Run No.	Duration Hrs.	Pressure psi	Velocity fps	Support[a]	Membrane[b]	20 Hours		100 Hours		200 Hours		400 Hours	
						R_{obs}[c]	J gfd	R_{obs}	J gfd	R_{obs}	J gfd	R_{obs}	J gfd
69	484	1000	18	0.45μ A	PAA+$FeCl_3$	80	20	74	28	71	28	65	30
	115		30	0.45μ A	PAA	42	64	(42)	(56)				
70	285	1000	30	0.025μ M	D50	60	12	60	11	63	11		
	285		30	0.45μ A	D50	25	77	27	37	30	24	Flux increased to 40 at 262	
	285		30	0.45μ A	Sephadex	50	90	51	72	54	69		
71	213	1000	30.5	0.025μ M	D50	67	7	67	6	66	6		
	213		30.5	0.45μ A	D50	59	54	64	35	57	23		
	213		30.5	0.025μ M	PAA+Zr(IV)	69	9	74	8	75	6		
	213		30.5	0.45μ A	PAA+Zr(IV)	59	74	74	62	71	55		
72	210	1000	30	0.45μ A	Primary	43	37	43	28	44	21		
	210		30	0.025μ M	Sephadex	56	13	58	12	64	7		
	210		30	0.45μ A	Sephadex	47	80	49	80	52	77		

*Secondary effluent; all others primary.

[a]A = Acropor, N = Nuclepore, M = Millipore.

[b]D50 = Low cross-linked Dowex-50; PAA = Poly(acrylic acid).

[c]All rejections are percentage chloride rejection.

[1]From Run 58T; [2]from Runs 58T and 59T; [3]from Run 67T.

TABLE 5

SUMMARY OF MEMBRANE PERFORMANCE AND OPERATING CONDITIONS AT AN OPERATING TIME OF 20 HOURS WITH SECONDARY SEWAGE IN THE STAINLESS STEEL LOOP AT Y-12 (C-LOOP)

Run No.	Operating Time with Sewage Hr.	Dynamic Membrane Additive	Membrane Support[b]	Pressure psi	Velocity fps	Results at 20 Hr R_{obs} (Cl^-) %	Results at 20 Hr Flux gfd
28	50	2	h	280	14	18	100
30	53	3	h	250	17	14	26
			*		31	16	10
			f		31	16	4
31	64	11	*	450	28	27	20
			h		17	22	42
32	144	10	h	500	16.5	23	88
	74		a	520	23	15	51
33	18		a	600	22	24	97
	90		h	500	14	26	71
35	95		h	520	14	23	59
	68	7[d]	h	520	14	25	68
36	49	13	e	600	45	50	115
	29	15	*	500	26	46	16
37	87	11	e	630	15	26	10
			h		14.5	43	56
38	22	15	*	1000	12	63	11
	71	9	h	465	4	7	53
	48	9	c	465	12	11	136
39	105	3[d]	h	750	14.5	37	140
			*		14.5	42	12
40	110	16[d]	h	750	14.5	30	66
			*		29	20	22
41	26	16[d]	h	760	14.5	29	87
			*		29	43	10
42	72	16[d]	h	800	14.5	32	75
43	13	17[d]	h	750	14.5	41	77
44	445	17[d]	h	760	14	43	72
45	15	7	h	760	17	30	108
46	113[c]	3	h	780	17	43	68
	92[c]	13	e		48	57	102

[a] Refer to Table 2 for additive identification.

[b] Refer to Table 3 for support identification.

* Membrane support was cellulose (mixed esters) designated Millipore VF with 0.025μ nominal pore size.

[c] Feed was primary sewage.

[d] Membrane additive was injected into feed stream during run.

better than the earlier results. Thus in Run 60, rejection was between 35 and 40% after 140 hours of operation at a flux of 40 gfd using a filter-aid coated hose as support and an axial velocity of 25 fps. Since there was evidence for end leakage, the rejections are probably less than could be achieved with better mounting. In a more recent 210 hour run at 1000 psi using an 0.45μ Acropor support, salt rejection was about 43% with flux of 40 gfd at 18 hours, but only 20 gfd at 210 hours when the axial velocity was 30 fps.

With the constituents of secondary sewage serving as membrane formers, observed salt rejections were somewhat lower (typically between 20 and 30%). This difference may not be significant since most of these experiments were carried out at a lower pressure (500-600 psi) and at least in one case rejection well in excess of 30% was obtained at a flux of ca 70 gfd when the axial velocity was 14 fps.

Systems with Continuous Addition of Additives

Most of the additives listed in Table 1 were tested with continuous addition of additive with and without preforming the membranes. Except in those cases where the membrane is essentially anion-exchange active, salt rejection in excess of 40% was obtained. Anion-exchange-active membranes were, in the presence of sewage, almost always inferior to the cation exchange membranes. Additive concentrations were usually 100 mg/ℓ or less. Except for the system using Leonardite in concentrations probably high enough to achieve complexing of polyvalent cations, salt rejection was relatively insensitive to concentration of additive used. In general, preforming the membranes gave better rejections, though with some sacrifice of flux. Organic rejections in these runs with secondary sewage were almost always better than 70% and frequently better than 80%.

Systems without Continuous Addition of Additives and with Preformed Dynamic Membranes

Because of the relative insensitivity of performance to additive concentration and the apparent improvement resulting from preforming, most of the later work was carried out in the absence of continuous addition. Membranes were dynamically formed from tap water with salt and additive. For several of these runs, the membranes were prepared under another (OSW-sponsored) program and then installed in loops operating on sewage. By the time these experiments were carried out, the mobile hyperfiltration loop at the sewage plant was in operation, allowing tests at the sewage plant with continuously replenished feed. Most of these later tests lasted for periods in excess of one week, and in a few, they extended to more than two weeks. Usually pressure was 1000 psi and sewage feed was spiked to 0.008 M NaCl.

Some of the most interesting membranes which seem to be operable without continuous addition are those prepared from homogenized low cross-linked ion exchangers (Dowex-50), from Sephadex, and from polyacrylic acid deposited on top of a hydrous oxide (e.g., Zr(IV), Fe(III)).

The experiments with Dowex-50 typically were carried out by passing a dilute (10 mg/ℓ) dispersion in tap water of the homogenized exchanger (Waring blender) over a porous support (e.g., Acropor AN). Membranes prepared in this manner typically have salt rejection in the range of 50-80% (0.01 M NaCl) and enormous fluxes (up to several hundred gfd) before exposure to sewage.

In one experiment with secondary sewage and a Dowex-50 membrane (Run 36, Table 5), carried out in the laboratory with feed trucked in at frequent intervals, salt rejection was 53% at 120 gfd after 8 hours; after 240 hours flux was still 70 gfd and rejection in excess of 50% when the axial velocity was 45 fps. Random measurements during the run showed total organic carbon rejections between 70 and 85%, the product containing 4-6 mg/ℓ; calcium plus magnesium rejection was 80% and turbidity rejection 95%.

A second long-term experiment was carried out in the corrosion-resistant loop in the laboratory with both primary and secondary sewage effluent trucked in. Salt rejections were 50 to 60% (similar to those in the run just discussed) irrespective if primary or secondary was used. Flux declined from 200 to 150 gfd during the first 50 hours, the last 20 of which were with primary. There was sharp flux decline (to 70 gfd) during a short period of operation at 10 ft/sec which was not completely recovered at later operation at 20 and then 44 fps. At shutdown (78 hours), flux was 92 gfd, chloride rejection – 58%, calcium and magnesium rejection – 76%, organic carbon – 82%, phosphate – 65%, and turbidity – 99%.

Because of the obvious importance of circulation velocity on flux, several experiments were carried out with Dowex-50 preformed membranes at the sewage plant with test sections operating simultaneously at different axial velocities. One such test lasted for 546 hours (Run 62, Table 4); axial velocities were 44, 31, and 18 fps. Chloride rejection was near 60% throughout the run at 1000 psi pressure. There was little difference in the fluxes of the membranes operating at the two higher velocities, but the membrane operating at 18 fps had considerably lower flux. In all three cases, flux declined with time, from initial values between 100-200 gfd to values between 40 to 60 gfd at 200 hours.

After 240 hours of operation, several techniques were explored for possible flux rejuvenation. A one-hour tap water wash increased fluxes significantly, but subsequent flux decline was rapid, so that within 24 hours the values had dropped to their prewash levels.

Since the fouling layer responsible for the flux decline probably contains negatively-charged polyelectrolytes from the sewage, which should be removable by base, flux rejuvenation was attempted with one-hour rinses with 0.1 M Na_2CO_3 and 0.1 M NaOH. The carbonate wash caused a large initial decrease in flux perhaps through carbonate precipitation; this was followed by an increase in flux. Fourteen hours after reexposure to primary sewage, fluxes were 84, 92, and 33 gfd for the test sections operating at 44, 31, and 18 fps, respectively, compared to values of 43, 42, and 23 gfd just prior to the wash. Flux decline was small during

the next 50 hours of operation. Before this run was terminated, after more than 500 hours of total operation (including several sodium carbonate and sodium carbonate and sodium hydroxide washes), fluxes were still 74, 84, and 37 gfd at these three velocities, chloride rejection was between 55 and 65%, turbidity rejection well in excess of 95%, organic carbon rejection 60 to 75%, phosphate rejection between 70 and 77%, and calcium and magnesium rejection near 85%.

We have also carried out extended tests with membranes prepared from polyacrylic acid, both with and without added hydrous oxides in the original preparation. In one of these experiments, with primary sewage effluents, rejections in general were higher and flux lower than with the Dowex-50 membrane. In this experiment, the membrane was prepared from a high molecular weight polyacrylic acid (Acrysól A5) in the presence of 5 mg/ℓ of iron (as $FeCl_3$). After an acid cycle (pH 4.5) (which seems to help to activate the membrane) rejection from primary effluent (containing 0.01 M NaCl) seemed to stabilize for 70 hours near 80%, but flux deteriorated to 20 gfd. Between 70 and 140 hours flux and rejection slowly declined. A base wash after 140 hours restored flux to ca 30 gfd but did not affect rejection (65-75%). Further base washes retained flux and rejection at this level for the next 220 hours (total 360 hours), but eventually caused deterioration of rejection. In this run, organic carbon rejection averaged near 85%, phosphate 89%, calcium and magnesium 88%, and turbidity removal in the later stages was in excess of 99%.

Very encouraging results were also obtained in a recent run in which a membrane was formed from a cation-exchange-active Sephadex (homogenized) deposited on 0.45μ Acropor. Pressure was 1000 psi and the primary sewage effluent was spiked with ca 0.01 M NaCl. After an initial induction period where flux was in excess of 100 gfd, flux stabilized at 80 gfd for well over 200 hours. Salt rejection remained constant during this period at ca 50%.

We believe we have now established technical feasibility of a sewage treatment process based on dynamically formed membranes. The results obtained with sewage are particularly gratifying since they show, together with our earlier studies on processing of pulp mill wastes, (8) that our hope that the method is applicable to a variety of pollution control problems is well founded. With respect to sewage, it now seems the method may not only provide a tertiary treatment, but that it might replace, in some cases, the relatively uncontrollable biological treatment (secondary) process. With a single hyperfiltration process, product superior to that from biological secondary treatment can be obtained. In a two-step process consisting of two hyperfiltrations or hyperfiltration combined with some other physical-chemical process (e.g., clarification, carbon adsorption), product quality sufficiently high for recycling of water might be achieved.

CONCLUSIONS AND RECOMMENDATIONS

It appears to us that the fluxes and rejections obtained, particularly with primary sewage effluents, were sufficiently encouraging to warrant continued examination of the process. Principal objective should now be development of a module.

While there is not yet sufficient information available for an economic analysis, development of information which would allow a meaningful cost estimate is now of prime importance. However, even in absence of such calculations a few generalizations can be made.

1. It is reasonable to expect that equipment costs per unit area for this process should be no more than, and perhaps less than those met in conventional hyperfiltration or reverse osmosis. Since fluxes are very much higher than so far reported for "conventional" hyperfiltration, total capital costs for this process will almost certainly be much lower.

The basic support structures for dynamic membranes are not more complicated and they may well be simpler, since rigid supports are not necessarily required. Flexible supports can probably be fabricated continuously in the lengths required for a plant. Further, the dynamic techniques avoid complications arising from conventional membrane casting operations and replacement costs of membranes might essentially vanish.

While support structures for dynamic membranes can in principle be cheap, the experiments reported here were carried out with designs which would be uneconomical for a plant. In future studies, it will become of great importance to identify a variety of cheap support structures and to test them, at least with the more promising dynamic membrane materials.

2. The experiments have been carried out largely at uneconomical axial velocities. The velocities were chosen to demonstrate that under some conditions, high flux operation is feasible. Minimum axial velocities for attractive fluxes have not been identified; this should become one of the principal objectives in continued studies. It will be necessary to identify hydrodynamic conditions which give the best compromise between energy consumption (pumping) and integrated flux (which determined equipment costs). Since chemical rejuvenation or backwashing and reforming of membranes is possible, the frequency of such rejuvenation must be optimized. Effectiveness of turbulence promoters for retarding flux decline should be evaluated.

3. Salt rejection by these membranes improves with increasing pressure. Towards the end of the program most experiments were carried out at 1000 psi. The economic optimum for pressure is not known although we doubt that it is as low as some of the literature on reverse osmosis with cellulose acetate would imply. Therefore we would recommend that

future work continue with average pressures near 1000 psi and that excursions to higher and lower pressures be carried out to acquire necessary information for economic analyses. Optimum pressures will probably differ for different situations with their different performance requirements.

While several dynamic membranes have been identified with which effective treatment of primary sewage can be achieved, there is continuing, low-priority need for examining other additives as information on their desalination capabilities becomes available. Since the effectiveness of the membranes will continue to improve as methods for membrane formation become better understood, some reexamination of previously considered membranes should be carried out. This is particularly true with respect to membranes formed from the sewage constituents themselves, which frequently showed significant salt rejection, and which may become completely adequate for treatment in some locations.

The most successful dynamically formed membranes so far found are essentially cation-exchange active. This implies that they should be sensitive to the presence of polyvalent cations. The municipal sewage used in these studies had a relatively low concentration of calcium and magnesium, ions which might interfere with proper operation of these membranes. In future studies, the tolerance limits of the membranes for these ions should be established in the presence of sewage constituents.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

Four test loops were used; three are stationary loops located in laboratory areas while the third is mounted in a trailer, located, for the present, at the Oak Ridge East Treatment Plant. One of the stationary loops ("Bench") is a small system, constructed mainly of stainless steel and titanium, similar to equipment previously described (7,10).

The other three loops were generally similar in design. Differences existed in the heat exchangers, instrumentation, feed pumps, and support equipment. The mobile and one of the stationary systems were constructed of stainless steel. In the other stationary loop, wetted surfaces were of titanium, hastelloy, or other materials of high corrosion resistance. Although both the stainless steel and titanium loops are "nominally" corrosion resistant, there was a small amount of corrosion in the stainless steel loop, particularly in the vicinity of welds. Consequently only the titanium loop was virtually corrosion resistant, thus permitting studies of additive chemistry with no interference from corrosion products. Because of this, the loops will be distinguished by material whenever this may have a bearing on the results.

Bench-type Hyperfiltration Loop

The small bench loop used for much of the preliminary membrane additive evaluation consists of a 5 gpm canned-rotor circulating pump, flow control valve, two test cells in series on the feed side, heat exchanger, basic instrumentation, pressurizer and an air-operated feed pump (11).

The test cells used with this loop consist of stainless steel housings enclosing the porous nickel disc used to support the replaceable "filter" (e.g., Millipore, or similar) on which the dynamic membrane is formed. The filter and cell are sealed with O-rings. Feed enters the cell through a central port, flows radially across the filter and exits through ports at the cell circumference. The hydrodynamics of the test cells are obviously quite involved and flow rate effects would probably not hold in a large scale loop or test cell. Consequently, flow rate was not a measured parameter. Feed velocity in runs with this loop was high enough to minimize concentration polarization; but may not have been sufficient to minimize membrane fouling.

Mobile Hyperfiltration Loop

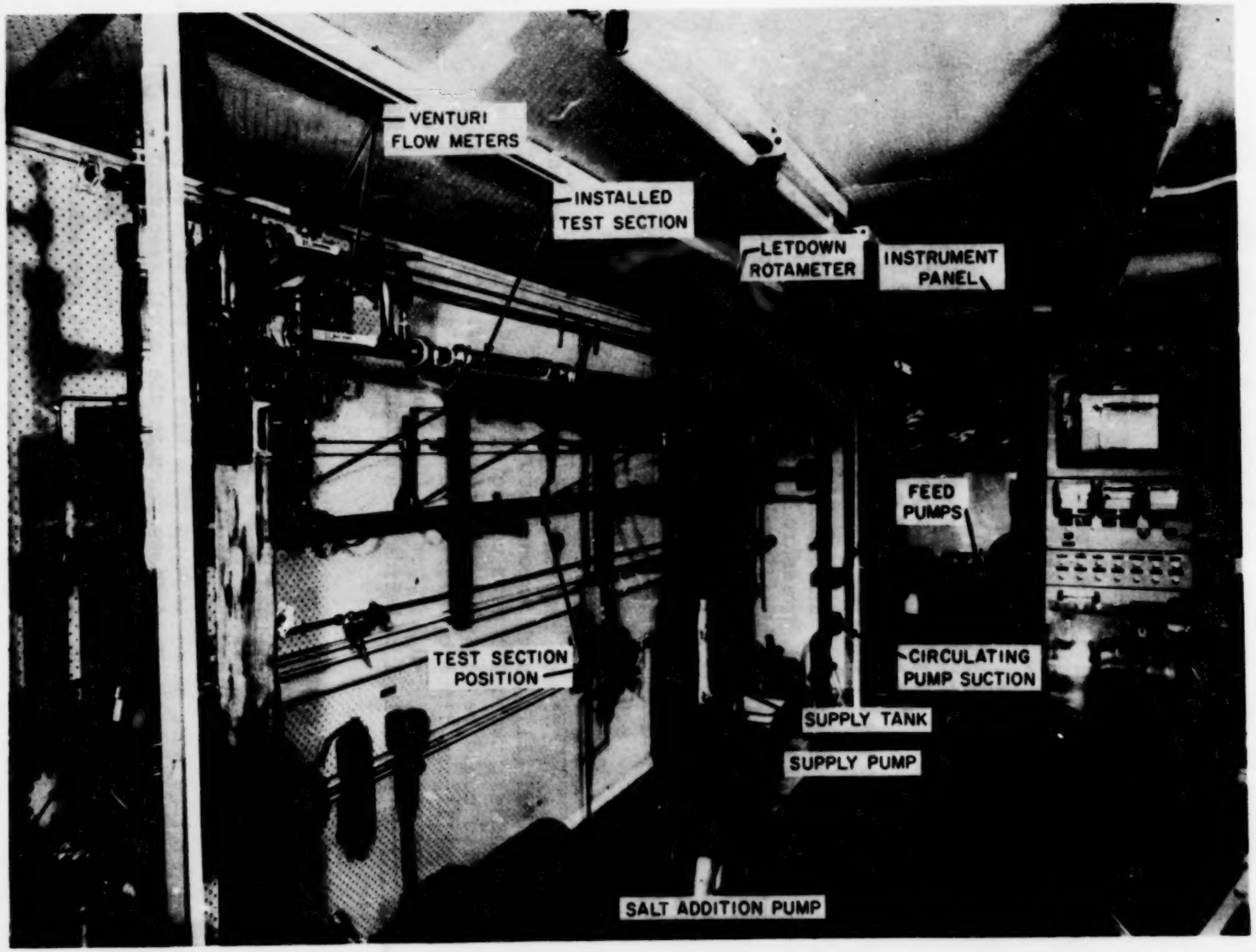
An interior view of the mobile hyperfiltration loop is shown in Fig. 1. The equipment is mounted in a highway trailer having internal dimensions of 6 1/2 ft x 7 1/2 ft x 28 ft. Feed circulation is provided by a canned-rotor, oil-cooled, pump rated 120 gpm at 294 ft head with 68°F fluid and pressure rated for 2000 psi, 600°F. This pump discharges through a tube-in-tube heat exchanger to three 1-in. test section connections. Flow through the two upper sections is manually controlled with ball valves and measured by parallel Venturis over the range 6 to 60 gpm. The lower test section is spare and presently isolated. A test section bypass is used for startup or at low flow rates. Pressurization and feed makeup are provided by a Mil-Roy Triplex feed pump rated 4 gpm at 2000 psi.

Auxiliary equipment consists of a cooling oil system for the circulating pump, product tank, feed pump supply tanks, transfer pump between product and feed tanks, and an air compressor. Chemical addition to the loop is through either an air operated piston pump – used for intermittent additions – or a small diaphragm pump – used for continuous addition and supplied by a 50 ℓ tank.

Sewage feed to the loop is provided by a skid mounted feed booster pump which takes suction from either downstream of the primary settling tanks or downstream of the secondary settling tanks.

Secondary effluent supplied by a second skid mounted pump is used for heat exchanger cooling water. In this particular instance fresh water is also connected to the heat exchanger as a reserve.

The only external support required is 75 kva of power at 230 volts and a small supply of fresh water for wash sinks (a hot water heater is installed).



Interior View of the Mobile Hyperfiltration System.

Figure 1

Instrumentation consists of readout and record of feed flow, temperature and pressure, automatic pressure control, and equipment alarm, protection and control devices.

Stationary 100 gpm Hyperfiltration Loop

A schematic flow diagram of the stationary 100 gpm loop at Y-12 is shown in Fig. 2. The canned-rotor circulating pump – rated 100 gpm at 294 ft head with 68°F fluid – discharges through a shell and tube heat exchanger to two parallel test sections. A Scott-Williams hydropulse feed pump – rated 5 gpm at 2000 psi – establishes loop pressure and supplies makeup feed. Primary auxiliary equipment consists of a cooling oil system for the circulating pump, a supply pump to return test section product to feed pump suction and a Sprague pump for injecting additives directly into the circulating feed stream.

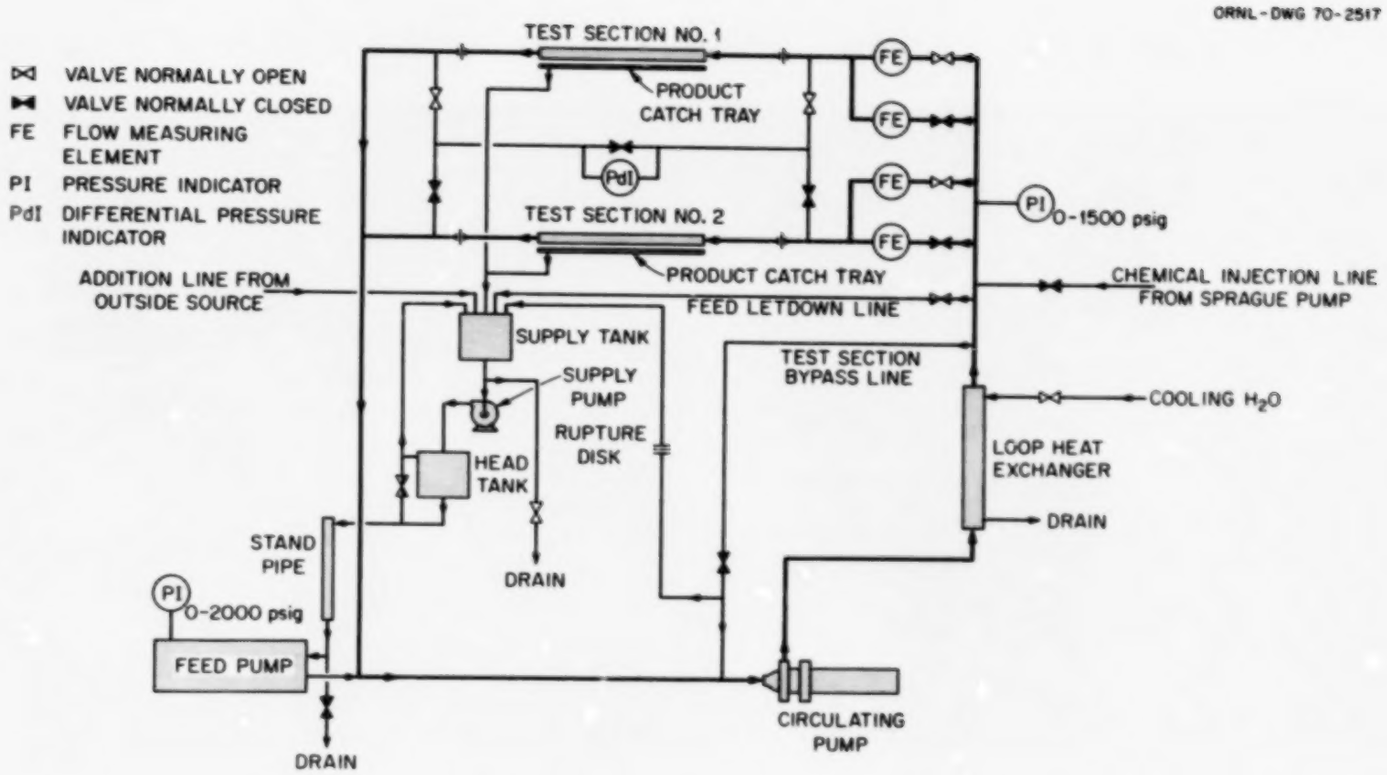
Instrumentation is minimal and consists of feed flow readout, feed temperature readout and record, pressure readout, pump parameter readout (volts, amps, power, operating time, power), and equipment protection and control devices. The loop will operate unattended and shuts down if parameters exceed set limits. Flow rate to each test section is measured with turbine flowmeters over the range 0-70 gpm. The readout instrument for the flowmeters is common.

Test Sections

In the bench loop, porous membrane supports were mounted in cells previously described (11), which expose about 1.5 cm^2 of surface to the feed. In most cases, two cells were connected in series in the loop, so that two supports could be tested simultaneously. Most of the porous supports were Millipore discs of average nominal pore size from 0.025 to 0.45 μ. In some cases, 0.45-μ Acropor AN (Gelman) discs were used; this material is porous poly(vinyl chloride co-acrylonitrile), reinforced by a woven nylon fabric.

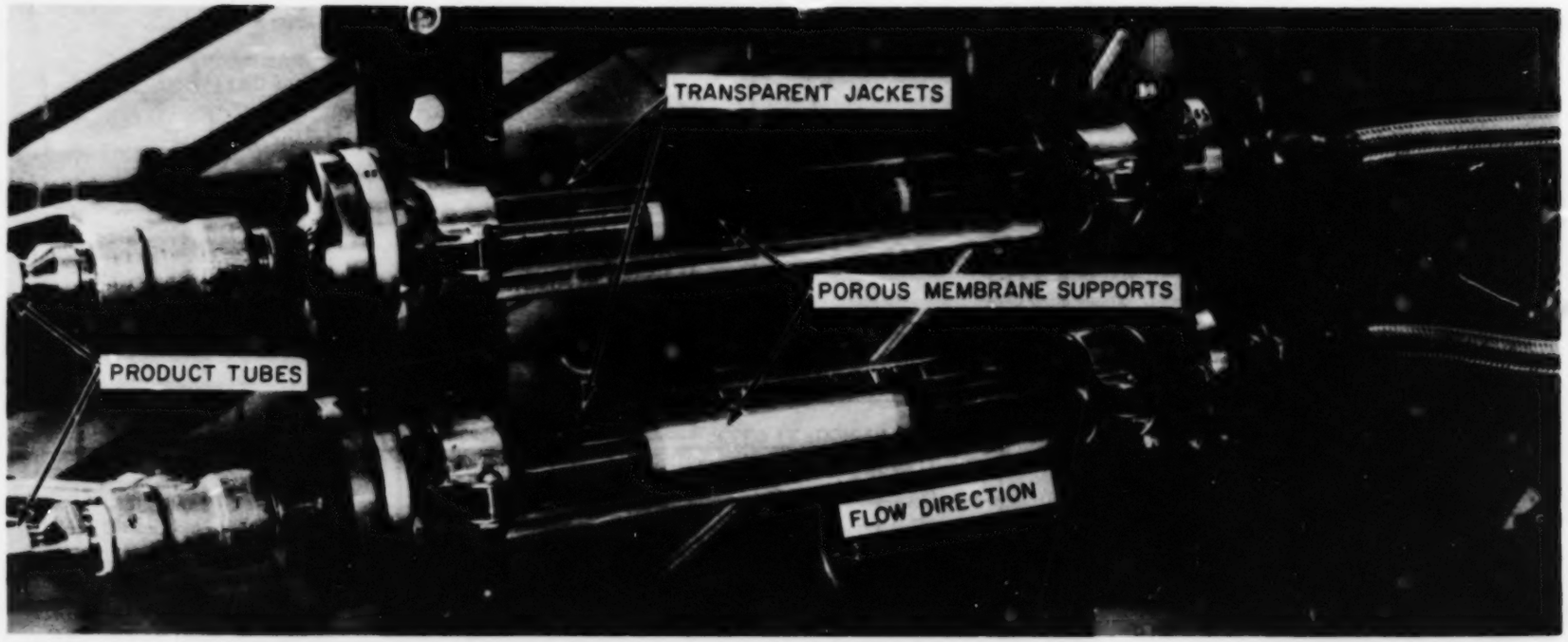
A variety of support structures was used with the large loops. Most attention will be given experiments with the test section design pictured in Fig. 3, which consists of a tube with a porous section enclosed in a transparent pressure jacket. A membrane support such as a sheet of Acropor AN or Millipore is wrapped over the porous stainless steel (usually 5-μ average pore size) section of a tube and sealed with pressure sensitive water-proof tape. Feed flows through the annulus between "finger" and jacket. The obvious advantage of these cells is visual observation of membrane condition throughout the run. These test sections have been used at pressures up to 1100 psi, but the transparent methacrylate jackets were limited – at these pressures – to room temperature feeds. (These are experimental test sections and are too expensive for use in a plant.)

Other supports used included a flat plate assembly (12) and a Selas 03 ceramic tube (0.9 μ), with pressurized feed in the annulus between



Schematic Flow Diagram of Typical Hyperfiltration Loop.

Figure 2



Hyperfiltration Test Section with Transparent Pressure Jacket.

Figure 3

jacket and finger (8). Another type, which was employed extensively and which has possibilities for practical application, was woven fabrics; specifically, we used reinforcing jackets for fire hoses (13). Hoses are pretreated with filter aid before dynamic formation of membranes (13,14). In some experiments, a 5-μ stainless steel sheet, mounted in the flat plate assembly, was similarly pretreated with filter aid.

Experimental Procedures

Membrane formation generally followed procedures proven in earlier studies (7). A solution of additive, at a typical concentration of 100 mg/ℓ, was circulated under pressure past the porous support under study. Membranes were also preformed from salt-water solutions or formed directly from sewage feeds. We utilized effluents from primary and secondary (activated sludge process) sewage treatment at the Oak Ridge East Plant. Composition of these effluents varied considerably from time to time. Organic carbon contents in primary effluents were generally between 50 and 100 mg/ℓ. Inorganic carbon contents were usually between 35 and 60 mg/ℓ; $Ca^{+2} + Mg^{+2}$, about 0.0015 M; and total phosphate, between 20 and 50 mg/ℓ. In secondary effluent, organic carbon was typically between 10 to 25 mg/ℓ. In several analyses by Oak Ridge Sewage Plant personnel in September 1967, the BOD values of secondary effluent averaged 24. Since Oak Ridge sewage is rather low in dissolved salts (usually < 0.001 M in chloride), salt was in many cases added (usually 0.008 M) to the sewage feeds. Addition of a salt spike provided a more realistic test of membrane properties under more typical conditions; since with ion-exchange membranes, rejection decreases with increasing feed concentrations, it tested the performance of the membrane under partially simulated high product recovery (fraction of feed recovered as product was very small in these experiments); and it facilitated analysis. Additive concentration during the preliminary survey was frequently maintained at a high level, rather than dropped to a few mg/ℓ, as in our usual procedure. High additive concentration probably facilitated the use of the organic carbon analysis as a measure of membrane integrity (absence of defects).

Additives

Additives were usually commercial or experimental polyelectrolytes (Table 2). Of those not so classifiable, "pulp mill wastes" refers to wash liquor generated in the sulfite pulping process, supplied to us by the Institute of Paper Research (Appleton, Wisc.) as a concentrate (8), "humic acid" refers to a material dissolved by soaking decayed oak leaves or pine needles, supplied to us by D. J. Nelson of the ORNL Health Physics Division; and Leonardite, an oxidized lignite, was supplied us by James L. Elder of the Grand Forks, N. D. Coal Research Laboratory, U. S. Bureau of Mines, and by A. J. Wittmaier of the Knife River Coal Co., Bismarck, N.D. Natural polyelectrolytes such as those found in pulp mill waste, humic acid or Leonardite, often are cation exchangers with the same sign as

sewage constituents. They they might be expected to have desalting properties similar to those found for commercial synthetic polyelectrolytes.

Analyses

Routine monitoring of salt (observed) rejection, $R_{obs} = [1 - (c_{product}/c_{feed})]$, usually expressed in percent, was by conductivity and by chloride analysis (interchangeably), with a Buchler-Cotlove chloridometer. At frequent intervals rejections of turbidity (Hach 2100 turbidimeter) and of organic and inorganic carbon (Bechman 915 total organic carbon analyzer) were measured; organic carbon is obtained from the difference between total carbon and inorganic carbon, both measured as CO_2. Occasionally, rejection of $Ca^{2+} + Mg^{2+}$ was determined by EDTA titration (Eriochrome Black T indicator), and of total phosphate by a colorimetric method using aminoapthosulfonic acid (15). Generally, chloride rejection was poorer than the rejection of other constituents, and thus serves as a minimum indicator of overall membrane performance.

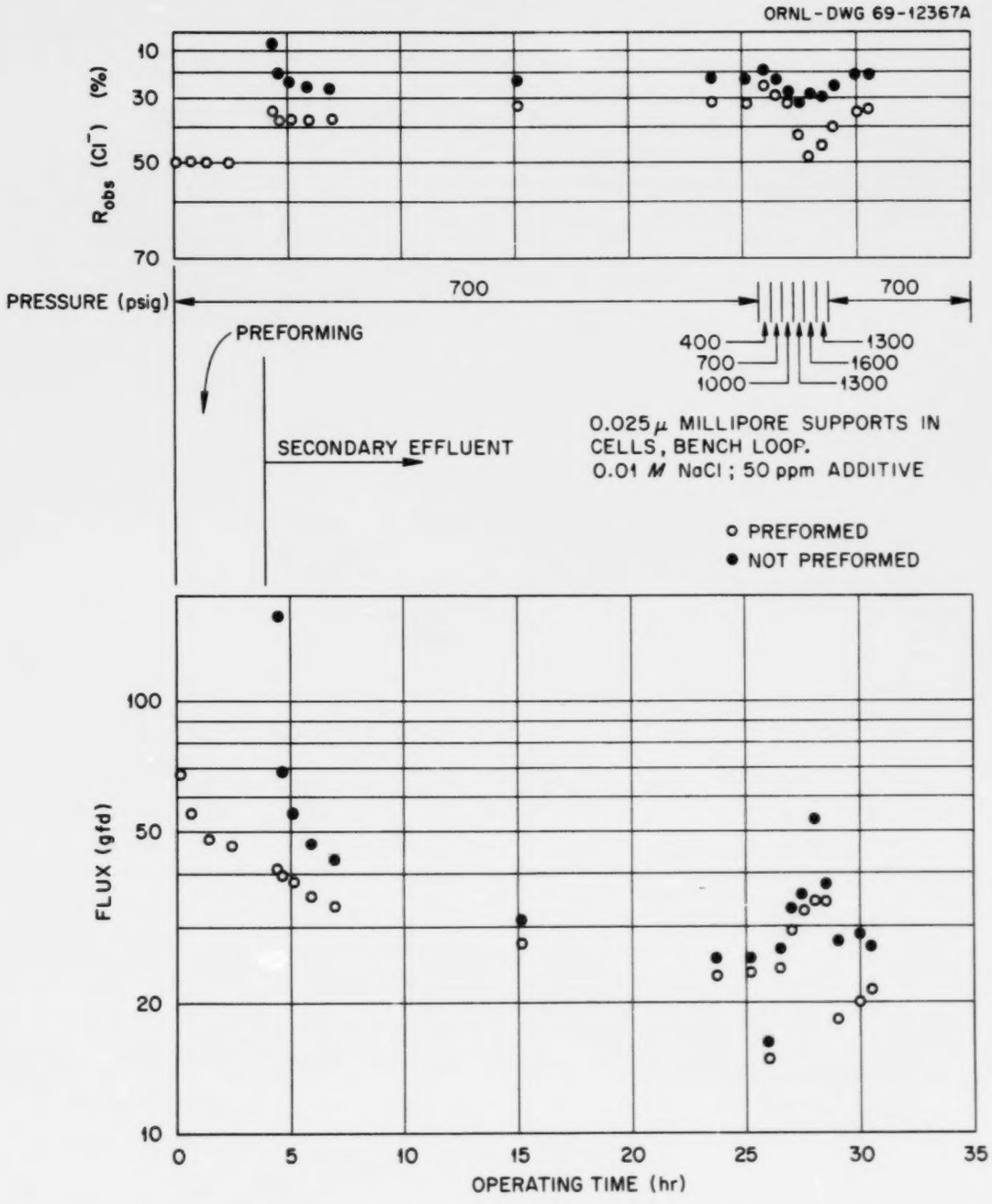
RESULTS

Preliminary Survey

It is not feasible to give here a detailed account of the results of the operating conditions in the preliminary survey of membrane forming additives for sewage treatment. These tests were usually of short duration, a day or so, and the majority were carried out in the bench loop; a typical example is given in Fig. 4. The switch from preforming feed to sewage effluent (containing additive) caused a sharp drop in rejection and a somewhat smaller decrease in flux. This behavior is typical and Table 6 gives some further examples (three with cation-exchange membranes and three with anion-exchange membranes). There are several possible explanations for decreases in rejection. Membrane polyelectrolytes may interact with polyelectrolytes or polyvalent ions of opposite charge sign in the feed. A layer of sewage constituents having lower rejection ability may form on top of the membrane and interfere with its performance. Although it is not clear what the correct explanation is, salt rejections by cation-exchange membranes are usually higher than by membranes formed from sewage feed constituents, which in turn frequently had higher rejections than anion-exchange membranes.

Plots of flux and rejection versus pressure show a large amount of scatter, but some trends which are apparent will be described below.

Anion-exchange vs Cation-exchange Membranes. Membranes (cation-exchange) formed with polyanionic additives in general reject salt more than those (anion-exchange) formed of polycationic additives. This relative behavior was not unexpected, since polymers in sewage are



Hyperfiltration of Effluent from Secondary Sewage Treatment with Dynamically Formed Poly(Maleic Acid) Membrane.

Figure 4

TABLE 6

TYPICAL EFFECTS OF SEWAGE EFFLUENTS ON HYPERFILTRATION BY DYNAMICALLY FORMED MEMBRANES (0.01 M NaCl IN SECONDARY EFFLUENT; BENCH LOOP, MILLIPORE SUPPORTS)

Additive[a]	Pressure, psig	Pore Size of Support μ	Rejection, R_{obs}, (Cl^-) %[b]		Flux, gfd[b]	
			Water	Sewage	Water	Sewage
1	700	0.025	50	38	46	30
3	600	0.025	52	40	28	19
6	700	0.025	77 (82)[c]	55 (78)[c]	14	7
22	600	0.025	48	25	17	7
24	700	0.025	40	15	43	28
25	700	0.025	70 (94)[c]	40 (73)[c]	90	65
25	700	0.45	62 (93)[c]	40 (70)[c]	70	55

[a] See Table 2 for additive identification.

[b] Measured within 2 hours before and after change from preforming to sewage feed.

[c] Parentheses indicate organic carbon; others, chloride.

probably primarily anionic, and would therefore tend to interact deleteriously with anion-exchange membranes. As we have already mentioned, however, rejections of cation-exchange membranes are also decreased on contact with sewage, though not so seriously as with anion exchangers.

Effect of Pressure. Rejections generally increase with increasing pressure, with a given additive, as well as with the group as a whole. Even with a membrane not affected by pressure, rejection is expected to increase with flux until a limiting rejection for the membrane is approached (10). However, here flux of "stabilized" membranes does not appear to increase with pressure, at least not proportionally. To a crude approximation, permeability appears to vary inversely with pressure. Changes in the membranes appear to result from aging while exposed to sewage feeds under pressure, and these changes may contribute to the increases in rejection with increasing pressure.

In short-term pressure excursions (an example is in Fig. 4), however, salt rejections and fluxes increase with pressure, and do not quite return to the previous values on the return to the original pressure at the end of the cycle. The effect of pressure is to some extent reversible, if the exposure is not too long.

Preformed vs Non-preformed Membranes. Table 7 lists eleven runs which compare performance during simultaneous operation with sewage feed of a membrane preformed from 0.01 M NaCl in water in one cell with performance of a membrane formed from secondary sewage effluent containing the same additive in the other cell. With cation exchangers, rejections by preformed membranes were almost invariably a little higher than nonpreformed while fluxes were a little to a great deal lower; with anion exchangers, performance was erratic. It was not clear from these results with the bench loop that preforming membranes from aqueous solutions of additives is in general advantageous. However, on the basis of results at the sewage plant, discussed below, preforming may lead to very attractive membranes, which may not require further additives for operation.

Pore Size and Support Effects. Rejections of membranes on 0.025-μ pore size do not appear to be appreciably higher than with those of 0.1 μ and up, and fluxes appear generally lower with the smaller pore size. A good comparison can be made from Table 8, which lists typical values measured simultaneously with supports of different sizes mounted in different cells during the same run. There is no convincing difference in rejections or fluxes between pore sizes in Table 8. Fluxes obtained in experiments in the bench loop seem in general to be low in compairson with the other systems. Reasons for this are not understood, since our desalination studies show no such consistent difference between cells and tubular arrangements.

A comparison between hoses and other supports is worth mentioning. In four cases in which runs were made with filter aid-pretreated hoses

TABLE 7

COMPARISON OF HYPERTILTRATION PROPERTIES OF PREFORMED MEMBRANES AND OF MEMBRANES FORMED OF POLYELECTROLYTES ADDED TO SEWAGE FEEDS (EFFLUENT FROM SECONDARY TREATMENT OF MUNICIPAL SEWAGE; 0.025 μ MILLIPORE SUPPORTS; BENCH LOOP; 0.01 M NaCl)

Additive*	Pressure, psig	Preformed		Not Preformed	
		R_{obs}, %	gfd	R_{obs}, %	gfd
1	700	30	25	20	28
2	700	39	40	33	50
3	600	43	16	38	25
3	700	55	42	50	50
4	700	35	14	30	45
5	700	30	25	30	35
6	700	50	30	40	35
11	700	50	29	40	32
22	600	30	10	25	50
23	600	10	23	20	35
24	700	8	25	5	28

*See Table 2 for additive identification.

TABLE 8

COMPARISON OF HYPERFILTRATION OF SECONDARY SEWAGE EFFLUENT BY MEMBRANES ON MILLIPORE SUPPORTS OF DIFFERENT PORE SIZES

Pore Size, Micron	Additive[a]	Pressure, psig	Preformed (A) Nonpreformed (B)	R_{obs}, (Cl^-) %	Flux, gfd
0.025	None	650	B	20	12
0.22				15	12
0.025	3	750	B	62	11
0.45				57	9
0.025	4	750	A	35	12
0.45				35	10
0.025	5[b]	725	A	30	30
0.45				30	30
0.025	6	700	A	55	4
0.45				70	6
0.22	26	750	B	40	16
0.45				40	14

[a]Identification of additives in Table 2.

[b]0.004 M $MgCl_2$ + 0.01 M NaCl in feed.

simultaneously with other supports, R_{obs} was higher in two cases with the hose, and in two cases with the other supports, while flux was higher in three cases with the hose, and in one with another support.

Generalizations about porous supports do not appear possible at this time and experiments to determine the best support for a given additive are necessary.

Organic Carbon Rejections. A better appraisal of the possibilities for removal of organic carbon can be made from the more extended experiments to be reported later, but some information of interest was obtained in the preliminary survey. As we implied earlier, because of possible low-molecular-weight organic constituents in sewage, organic rejections are doubtful indices of absence of membrane defects. In addition, with secondary effluent feeds which did not contain additional additives, organic carbon was frequently rather low in effluents, and analyses uncertain.

Rejections of organic carbon (the sum of that originally in the feed and the polyelectrolytes added to form membranes) are usually higher than salt rejection. Of twelve runs at pressures above 550 psi, in which measurements were made with supports of 0.1-μ pore size and larger, organic carbon rejection was 70% or higher in eight. In two of the other four, low salt rejection indicated defective membranes. One other was anomalous in that chloride rejection (65%) was greater than organic rejection (35%). Below 550 psi, organic carbon rejections were between 55 and 75%, but all values were well above the corresponding salt rejections.

With 0.025-μ supports, seven of eight measured organic carbon rejections were between 65 and 95%, and all of these were higher than the corresponding salt rejections. The exception was additive 8 at 1000 psi for which organic carbon rejection was 57%, about 10% less than chloride rejection.

With a filter aid-pretreated hose jacked mounted in the stainless steel stationary loop, a membrane formed from corstituents of secondary effluent feed usually rejected 70 to 80% of organic carbon, while chloride rejections scattered around 30%. Fluxes were 50 to 80 gfd and pressures were 500 to 800 psi.

Summary. It appeared that additives forming cation-exchange membranes are more promising for sewage treatment than those forming anion exchangers. Of the cation-exchange class, polyacrylic acid and homogenized low-cross-linked polystyrene sulfonate cation-exchange beads (Dowex-50) looked particularly promising, though some others could not be excluded completely. Despite rather wide scatter, salt rejections from primary effluents seemed not much less than from secondary. Salt rejection appeared to be improved by operation at higher pressures, with membranes formed from sewage constituents, as well as from intentional additives. The results also suggested that filter aid-pretreated fabric hoses may be useful with some additives. It appeared that formation of membranes by putting additives directly into sewage is possible.

Long-Term Runs with Secondary Effluent

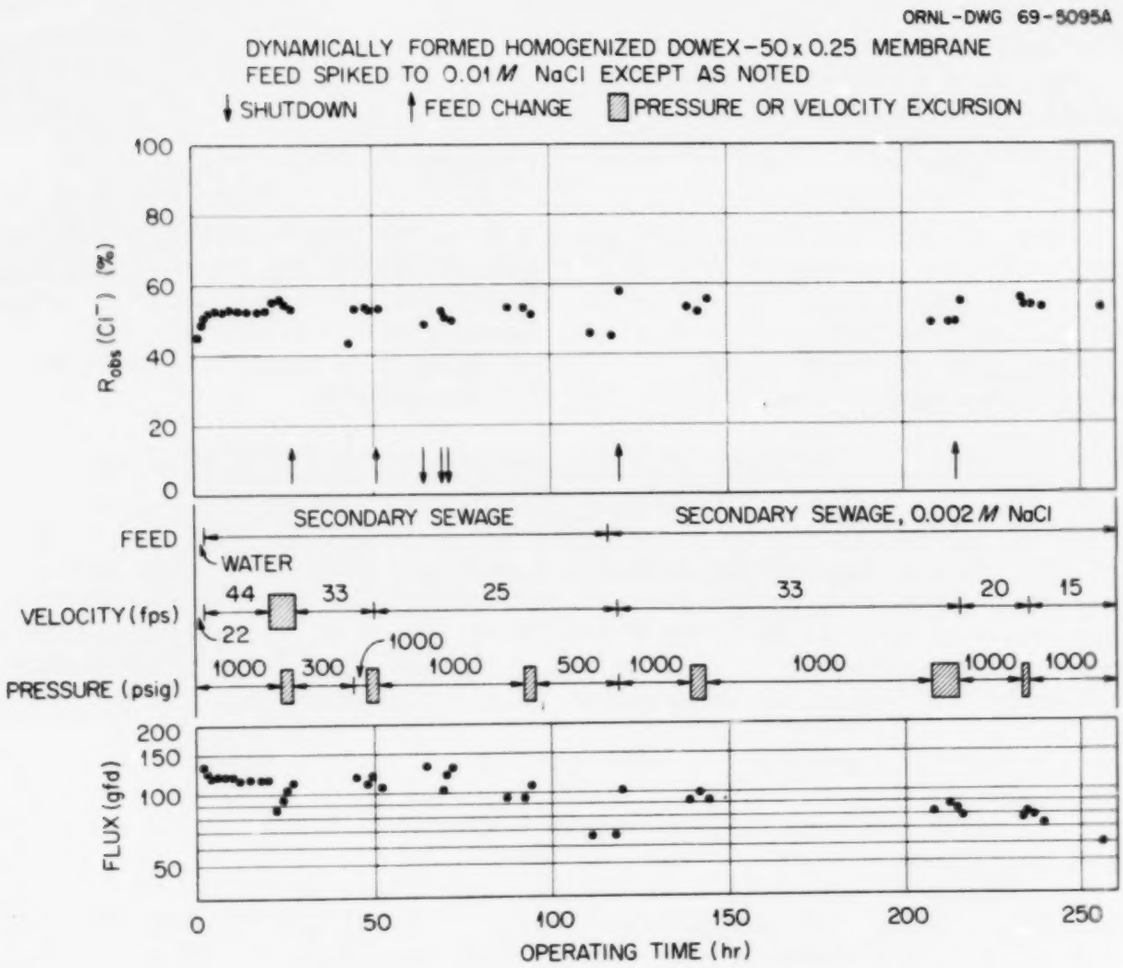
We report in some detail longer-term runs which were carried out with some of the more promising additives (homogenized cation exchangers, homogenized Sephadex, polyacrylic acid). In essentially all of these runs, the additives were only present during the formation step. Except when hoses were used or when otherwise noted, the test assemblies were wrapped porous stainless steel fingers, in Lucite jackets, on which dynamic membranes were preformed in the "titanium loop"; when necessary, these were transported to other loops, e.g., the mobile loop at the sewage plant.

Not all aspects of our procedure are as yet under control, and thus even ignoring variations in the composition of the sewage, differences in observations in the various runs are to be expected. However, we believe that the histories of the runs presented illustrate the capabilities of these dynamically-formed hyperfiltration membranes in sewage treatment at the present stage of development.

Treatment of Secondary Effluent with Homogenized Low Cross-Linked Ion Exchange Membranes. Since the procedure in this test is in many ways typical of the others to be reported, we shall describe it in some detail. It was carried out with the stationary corrosion-resistant (titanium) loop with sewage feeds brought in to the laboratory. Test sections were similar to those shown in Fig. 3; 0.45-μ Acropor AN sheets were wrapped around 5/8-in.-OD porous stainless steel tubes, which were inserted in 25/32-in.-ID transparent pressure jackets.

Before this experiment, membranes were formed in separate runs from the cation exchanger, Dowex-50 X 0.25, and the anion exchanger, Dowex-1 X 0.25, which had been homogenized in a Waring blender. The preforming feed solutions contained 10 mg/ℓ of the additive, and in the case of the anion exchanger, were 0.05 M in $NaClO_4$, and of the cation exchanger, 0.025 M in $MgCl_2$. The perchlorate form of Dowex-1 and the magnesium form of Dowex-50 are much less swollen than the chloride and sodium forms; after deposition of the resin on the porous support, change to NaCl media might be expected to swell the particles to fill the pores snugly. Although we still use a perchlorate solution to form Dowex-1 membranes, in subsequent tests the $MgCl_2$ step, in comparison with formation from NaCl solutions, has not appeared to be beneficial with Dowex-50. After changing to 0.05 M NaCl with 1 mg/ℓ additive, salt rejection by the anion exchanger was 58% at 100 gfd (1000 psi), and by the cation exchanger, 57% at 150 gfd.

With both sections installed in the loop, in a preliminary test with 0.01 M NaCl (no additive was used here or subsequently), R_{obs} for the anion exchanger was 64% at about 300 gfd, and for the cation exchanger, 45%, at about 400 gfd (results with the cation exchanger are summarized in Fig. 5, though the flux of the point just mentioned is off scale and



Hyperfiltration of Effluent from Secondary Treatment of Oak Ridge Sewage.

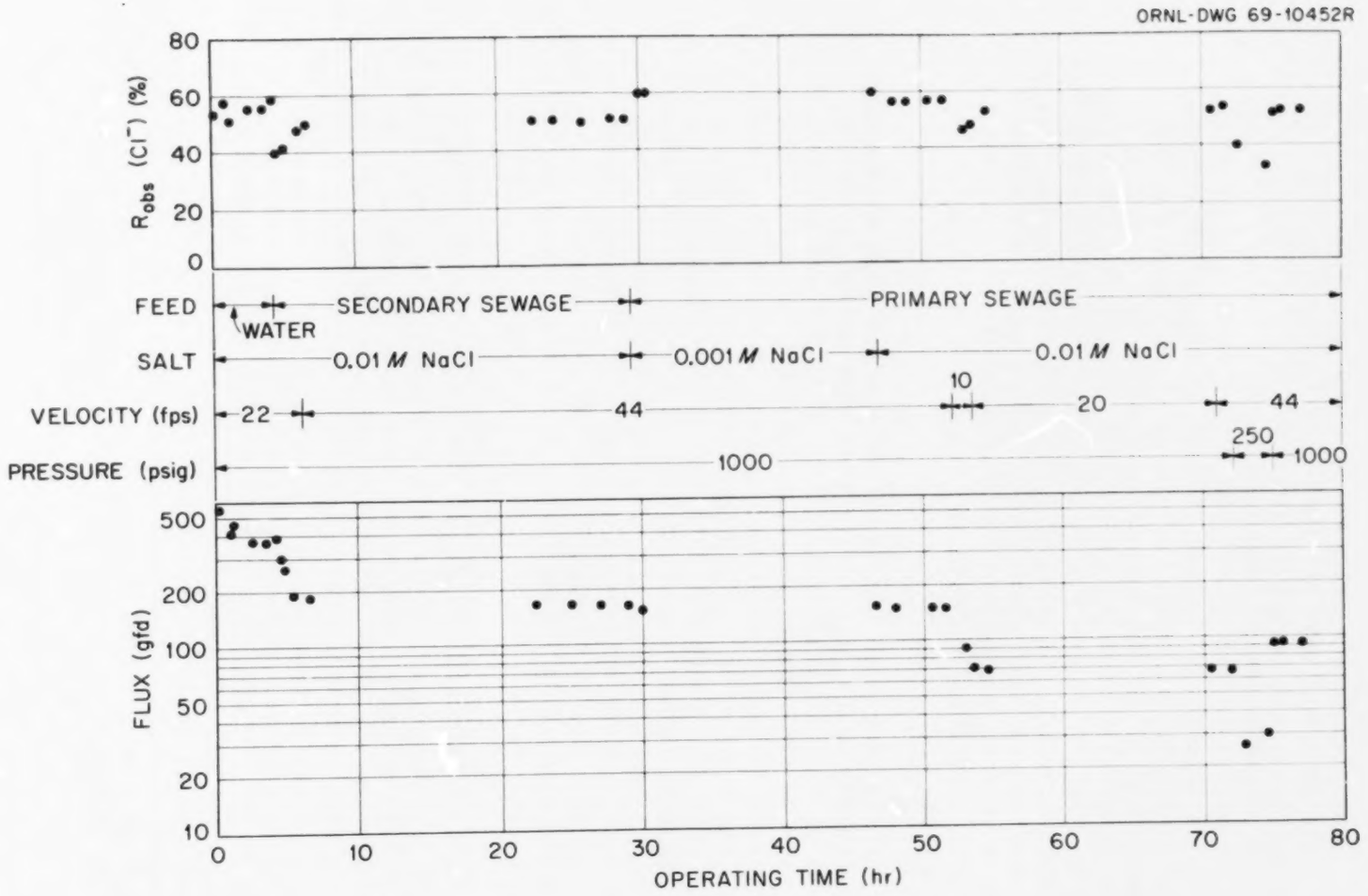
Figure 5

is not shown). Secondary sewage effluent was then introduced with 0.01 M added NaCl. There was an immediate darkening of the surface of the anion-exchange membrane, but no appreciable change in appearance of the other membrane; presumably sewage components were sticking to the surface of the anion exchanger, which has positive fixed charges, more readily than to the negatively charged surface of the cation-exchange membrane. After one hour, rejection of the anion-exchange membrane had dropped below that of the cation-exchange membrane, to 40% (120 gfd), compared to 49% (130 gfd). In eight hours, R_{obs} for the cation-exchange membrane was 53% at 120 gfd, while the anion-exchange membrane had seriously deteriorated, its rejection being only 14% at 200 gfd. These results confirm the indication of the preliminary survey that cation-exchange membranes are better for sewage treatment than anion-exchange membranes. We shall discuss the results with the anion exchanger no further.

The run continued for over ten days. Except for some measurements at pressures below 1000 psig, salt rejections were mostly above 50%. Flux decline was gradual at axial velocities of 20 fps and up after 240 hours, fluxes were 70 gfd. At 15 fps, flux decline was rapid. There were four changes in feed with no marked changes in rejection, except when added salt was dropped to 0.002 M NaCl. With this initial concentration, the feed was concentrated to 50% of its original volume by discarding product, rather than returning it to the feed container (Fig. 5, 120 to 215 hours); no marked effects of feed concentration were noted. Random measurements were made of other constituents: organic carbon rejections were mostly between 70 and 85%, the product containing 4 to 6 mg/ℓ; rejections of $Ca^{2+} + Mg^{2+}$ were about 80%; and of turbidity, about 95%.

Comparison of Hyperfiltration of Primary and Secondary Effluents by a Dowex-50 X 0.25 Membrane. Tests in the titanium stationary loop of a cation-exchange membrane, similar to that just discussed, with effluents from primary and of secondary treatment of sewage are summarized in Fig. 6. Salt rejections were similar to those of Fig. 5 and were as high from primary feeds as from secondary, under comparable conditions. Fluxes declined on introduction of secondary effluent, but remained high, 100 to 200 gfd, for the first fifty hours, including 20 hours exposure to primary effluent. A sharp decrease in flux, to 70 gfd, occurred during a short period of operation at 10 fps, and the initial flux was not regained during subsequent operation at higher velocities. Some restoration of flux occurred after a period of operation at 44 fps at 250 psig. At shutdown (78 hours) flux was 92 gfd, and R_{obs} was for chloride, 58%; for $Ca^{2+} + Mg^{2+}$, 76%; for inorganic carbon, ~59%; for organic carbon, 82% (the product contained 15 ppm); for turbidity, 99%; and for total phosphate, 65%.

As in the previously described run, an anion-exchange membrane was in parallel with the cation-exchange membrane, but its performance relative



Run 48: Hyperfiltration of Sewage Effluents
(Dowex-50 x 0.25 Membrane on 0.45 μ Acropor Support, 75°F).

Figure 6

to the cation exchanger was generally similar to that in the previously described test, and details will not be reported. Darkening of the anion-exchange membrane surface on exposure to sewage was not as marked as in the previous experiment.

Two-stage Treatment. It would conceivably be worthwhile to improve a hyperfiltration product by a second-stage treatment. We have done little work aimed at evaluating this possibility, but a second step in a bench loop using as feed the product collected from the primary sewage phase of the run in Fig. 6 suggests that the procedure may be useful. The membrane was preformed of starch sulfate (additive 7, Table 2) on 0.45-μ Acroport AN and on 0.025-μ Millipore supports, in cells. Membrane formation was poor on the 0.45-μ support, R_{obs} = 23% of 0.01 M NaCl in water, and only the results with the Millipore, which rejected 81% of salt at flux 60 gfd (1000 psig), will be discussed. Part of the primary product (0.0055 M NaCl) was tested with 10 mg/ℓ starch sulfate added. Rejection was 72% and flux 45 gfd. A second portion was tested without additive, the value of R_{obs} being 69% at the same flux.

The decrease in rejection occurring on addition of hyperfiltration-treated primary sewage effluent was not as great as generally occurs on addition of primary or secondary effluent. Apparently, the first hyperfiltration step removed much of the material interferring with desalting properties of the membrane.

Long-Term Runs with Primary Effluents

Practically all studies with primary sewage effluents were carried out at the Oak Ridge East Sewage Plant with the mobile hyperfiltration loop. Most of these runs extended for more than 100 hours. As mentioned earlier, except for one run with hose and another using sewage constituents, the membranes were preformed on porous material wrapped on porous stainless steel supports in the titanium loop and the assemblies transported to the sewage plant. After the preforming step, no further additives were used.

Table 9 summarizes the runs, support structures and principal operating conditions. Table 4 summarizes flux and rejections at representative times during the runs. Except when otherwise noted, the feed was "spiked" to 0.008 M NaCl.

Runs 58, 59, 60; Dowex-50 and Self-rejecting Membranes. These three runs are described together because the same membrane "C" was used through all the runs for total operating times of 56 hours with secondary and 158 hours with primary sewage feed. Runs 58 and 59 operated at 1000 psi and Run 60 operated at 730 psi feed pressure.

In Run 58 supports used were Acropor (0.45μ) (A and C) and Nucleopore (B). The feed was (unspiked) secondary sewage renewed at a rate of 2 gpm which contained 0.8 meq/ℓ chloride, 12.5 mg/ℓ organic carbon, 52 mg/ℓ inorganic carbon, 0.0013 M Ca plus Mg and a turbidity of 13 JTU. Membrane performance after 8 hours of operation is shown in Table 10.

After 11 hours, a 4-1/2-day shutdown occurred and Membrane A failed. Seven hours after restart, chloride rejections were 34% (B) and 53% (C) at fluxes of 64 and 149 gfd, respectively. At 29 hours the tape seals of A and B failed; rejection by C was 51% at 99 gfd. At 54 hours rejection by C had increased slightly to 55%; flux was 92 gfd. At 56 hours the run was terminated.

Use of Membrane C (on 0.45μ Acropor from Run 58 was continued in Run 59) with (unspiked) primary sewage feed which contained 0.62 meq/ℓ chloride, 33 mg/ℓ organic carbon, 62 mg/ℓ inorganic carbon, 0.0014 M Ca plus Mg and a turbidity of 20 JTU. Membrane performance after an additional 8 hours of operation is shown in Table 11.

At 33 hours chloride rejection was 65% at 78 gfd. After 42 hours with primary (total time 98 hours) the run was terminated.

The same D-50 membrane which was used in Runs 58 and 59 was again used in Run 60 in parallel with a "natural" membrane on a fiber hose precoated with filter aid. The primary sewage feed (unspiked) contained 0.72 meq/ℓ chloride, 80 mg/ℓ organic carbon, 49 mg/ℓ inorganic carbon, 0.0013 M Ca plus Mg and a turbidity of 40.3 JTU. Membrane performances after 8 hours of operation are listed in Table 12.

TABLE 9

MATERIALS AND OPERATING CONDITIONS FOR RUNS OF OVER 100 HOURS WITH PRIMARY SEWAGE

Run Number	Material		Feed Velocity (fps)	Feed Pressure (psi)	Duration of Run (hrs)
	Membrane	Support			
58, 59, 60	D50	A	44	1000 & 730	214
60	None	Hose	25	730	141
61	D50	A	44	1000	128
	PAA	A	44	1000	128
62	D50	A	44	1000	546
	D50	A	31	1000	546
	D50	A	19	1000	546
66	D50	A	44	1000	108
	D50	A	18	1000	108
67	D50	A	44	1000	391
	D50	A	31	1000	391
67 & 68	D50	A	18	1000	505
67	D50	A	13	1000	174
68	PAA+Fe(III)	A	18	1000	114
69	PAA+Fe(III)	A	30 & 20	1000	500
	PAA	A	30	1000	115
70	D50	M	30	1000	290
	D50	A	30	1000	290
	Sephadex	A	30	1000	290
71	D50	M	30	1000	222
	D50	A	30	1000	222
	PAA+Zr(IV)	M	30	1000	222
	PAA+Zr(IV)	A	30	1000	222
72	None	A	30	1000	214
	Sephadex	M	30	1000	214
	Sephadex	A	30	1000	214

Notes:

D50 = Homogenized Dowex-50 cation exchange resin, 1/2% cross linked.
PAA = Poly(acrylic) acid.
A = Gelman Acropor AN 450 (0.45-μ pore size).
M = Millipore VF (25-mμ pore size).

TABLE 10

PERFORMANCE OF DOWEX-50 ON 0.45μ ACROPOR (A,C) AND 0.45μ NUCLEPORE (B) WITH UNSPIKED SECONDARY SEWAGE AFTER 8 HOURS OPERATION (RUN 58)

Tube	Flux (gfd)	Observed Rejection (%)				
		Chloride	Organic Carbon	Inorganic Carbon	Ca + Mg	Turbidity
A	110	68	82	65	85	96
B	82	42	74	52	62	92
C	149	54	60	62	85	94

TABLE 11

PERFORMANCE OF DOWEX-50 ON 0.45μ ACROPOR WITH UNSPIKED PRIMARY SEWAGE (CUMULATIVE RUNNING TIME 64 HOURS) (RUN 59)

Flux (gfd)	Observed Rejection (%)				
	Chloride	Organic Carbon	Inorganic Carbon	Ca + Mg	Turbidity
81.5	66	86	78	93	91

TABLE 12

PERFORMANCE OF SEWAGE MEMBRANE ON HOSE AND D50 MEMBRANE (UNSPIKED PRIMARY SEWAGE 8 HOURS AFTER STARTUP; CUMULATIVE RUNNING TIME 106 HOURS FOR D50) (RUN 60)

Test Section	Flux (gfd)	Observed Rejection (%)				
		Chloride	Organic Carbon	Inorganic Carbon	Ca + Mg	Turbidity
Tube	124	58	89	58	77	96
Hose	184	31	78	34	54	93

It should be noted that the tube flux given in Table 12 (124 gfd) is significantly higher than its flux – given in Table 11 as 81.5 gfd – some 12 hours earlier in the membrane history; rejection is somewhat lower (58% vs 66%). As often observed, pressure cycles due to shutdown and restart effect some rejuvenation of the membrane.

Chloride rejection of the D-50 membrane held relatively steady over the next 65 hours; flux was 96 gfd after a 34-hour period and 76.8 gfd over a following 31-hour period.

Rejections of the "natural" membrane on the hose section held relatively steady over a 31-hour period following results of Table 12, but flux decreased to ca 70 gfd. At shutdown, after 141 hours of operation, chloride rejection was 38% at 76 gfd.

Run 61; Dowex-50 and PAA-Amberlite IRC-50 Membranes. One test section used preformed Dowex-50 X 0.5 membranes on both sections (A and B) of a double finger wrapped with 0.45μ Acropor with different methods used to install the Acropor. Another "finger" used an Amberlite IRC-50 precoat followed by PAA on a 25-mμ Millipore support. After 2 1/2 hours of operation with tap water, feed was changed to primary which contained 0.54 meq/ℓ chloride, 60 mg/ℓ organic carbon, 51 mg/ℓ inorganic carbon, 0.0014 M Ca plus Mg, 26 total mg/ℓ PO_4 and a turbidity of 29 JTU. Table 13 gives results for a set of samples taken at 22 hours.

The PAA-Amberlite IRC-50 membrane on 25 mμ Millipore exhibited very low product flux; rejections were not appreciably higher (until flux dropped to < 6 gfd) than for the D-50 membranes tested in the same run.

Run 62; Effect of Velocity and Base Washes on Dowex-50 Membranes. Three Dowex-50 X 0.5 membranes preformed on 0.45μ Acropor were exposed to primary sewage spiked to 0.008 M NaCl, for 550 hours. Feed velocities for the three membranes were 44 fps, 31 fps, and 19 fps to determine the effect of feed velocity on flux and rejection. During the later part of the run, various chemical rejuvenation techniques were examined. The run is summarized in Fig. 7.

Salt rejections over the run scattered around 60% at the 1000 psig pressure used most of the time. The membranes survived several shutdowns without apparent damage. In the first three hundred hours fluxes were higher for the higher circulation velocity; the differences between the 44 and 31 fps membranes became less with time. Fluxes at 18 fps were considerably lower than those at the higher rates. Fluxes declined from initial values of 100 to 200 gfd to 40 to 60 at 20 hours.

In an effort to rejuvenate the membranes (at 240 hours), tap water was circulated in the system for ca one hour. There was some increase in flux, at least at 44 and 31 fps, but fluxes declined rapidly to the values just before the wash.

Since the fouling layer thought to be responsible for the flux decline is probably composed of various negatively charged polyelectrolytes

TABLE 13

MEMBRANE PERFORMANCE AFTER 22 HOURS OPERATION WITH UNSPIKED PRIMARY SEWAGE (RUN 61)

Flux (gfd)	Observed Rejection (%)					
	Chloride	Organic Carbon	Inorganic Carbon	Mg + Ca	Turbidity	Total PO_4
122[a]	64	62	64	71	95	67
9.4[b]	72		78	86	89	37

[a] D-50 Membrane.

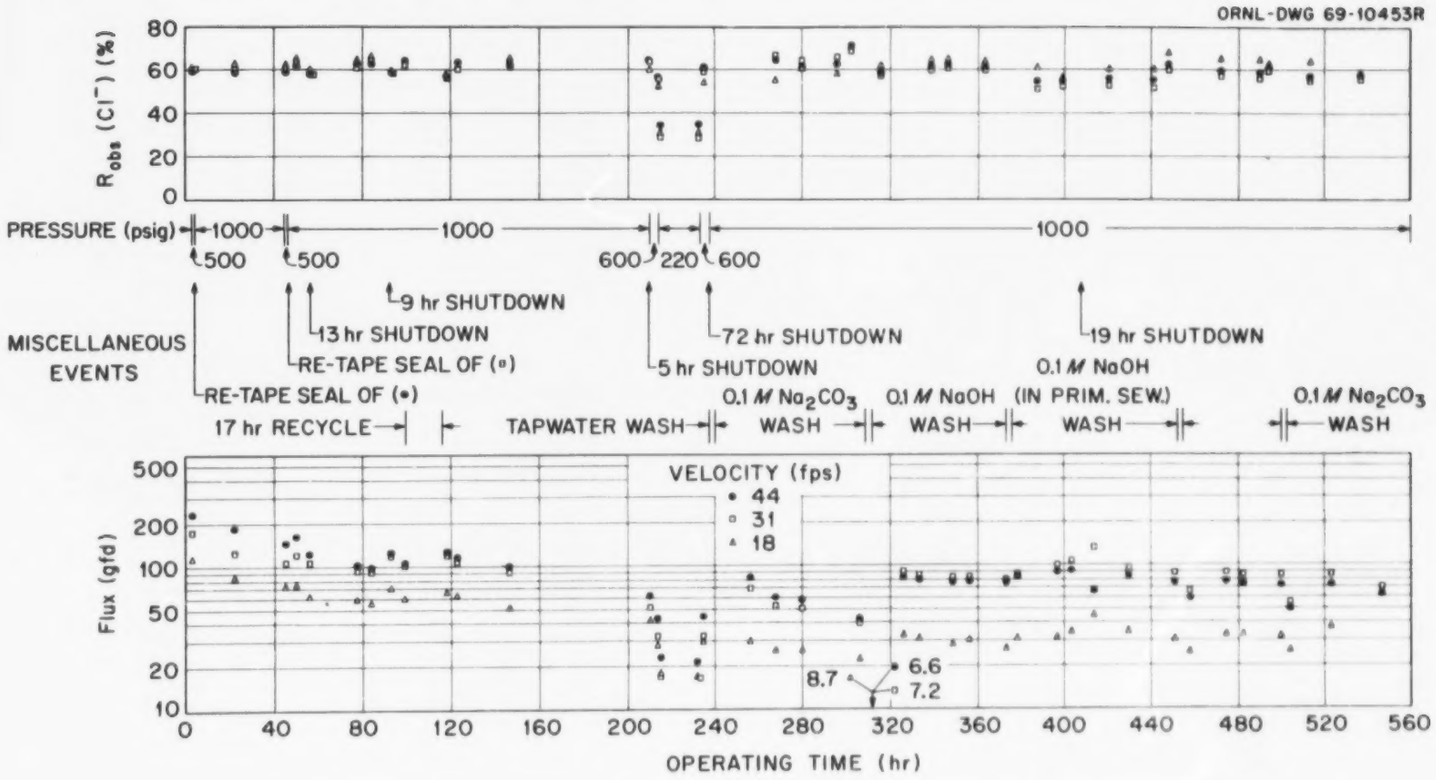
[b] PAA-Amberlite Membrane.

present in sewage, a basic wash was hoped to be more effective than water. Consequently, the loop was then rinsed with tap water and washed with 0.1 M Na_2CO_3 in water for 1 hour. For reasons not yet established, but likely associated with precipitation of carbonates following return to primary sewage, fluxes decreased very rapidly to less than 10 gfd, but then recovered overnight to values higher than pre-wash fluxes. After 14 hours, fluxes were 84, 92, and 33 gfd compared to 43, 42, and 23 gfd just prior to the wash. Flux declines over the 64-hour period following this wash were modest (Fig. 8, lower left corner).

At 373 hours the loop was again rinsed with water and washed with 0.1 M NaOH for 45 minutes. During the NaOH wash, fluxes increased by ca 50% and there was a very noticeable removal of the black components of the crud layer that had formed on the membranes during operation. At the end of the wash period, membrane appearance was very similar to that at the beginning of the run. Crud removal was not visually observed with either the water or Na_2CO_3 washes. With the change to primary feed, there was an initial flux decrease followed by increasing flux over the next 27 hours (Fig. 8, lower center). Membrane performance just prior to the wash and at 27 hours after the wash is given in Table 14.

At 452 hours a one-hour recycle of primary sewage spiked to 0.1 M NaOH was completed. Fluxes increased during the recycle, but immediately decreased with the change back to primary sewage feed (Fig. 8, lower right). At 46 hours after the wash, fluxes and rejections were only slightly different from those prior to the wash. Results in order of decreasing circulation velocity were: 70, 84, 30 gfd and 59%, 57% and 65% rejection.

A second Na_2CO_3 wash was completed at 501 hours. Following change back to primary feed, we observed an initial flux decline followed by a



Run 62, Hyperfiltration of Primary Sewage Effluents with 0.01 *M* NaCl Spike (Dowex-50 x 0.5 Membrane on 0.45 μ Acropor Support, 100°F).

Figure 7

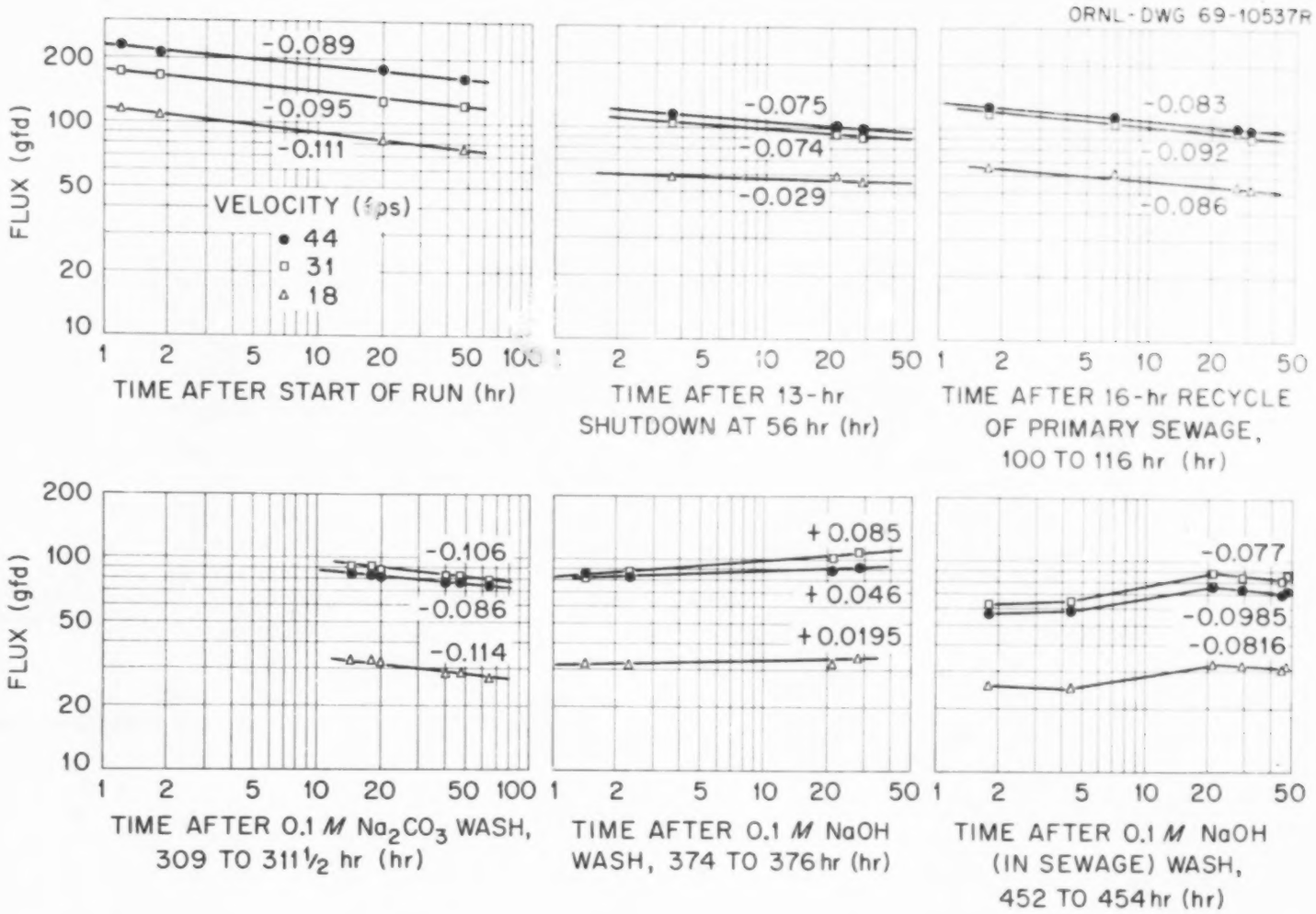


Figure 8. Hyperfiltration of Primary Sewage Effluent. Behavior of Flux Following Various Events (numbers with each curve are slopes of curves)(Run 62: Dowex-50 x 0.5 membrane on 0.45μ support, 1000 psi, 100°F).

TABLE 14

EFFECT OF FIRST NaOH WASH AT 373 HOURS

Elapsed Time After NaOH Wash, Hr	44 fps		31 fps		18 fps	
	R_{obs}, %	Flux gfd	R_{obs}, %	Flux gfd	R_{obs}, %	Flux gfd
-1	61	75	61	79	65	27
+27	56	94	55	110	64	35

flux increase and then a second decline. The initial flux decline was less pronounced than after the first Na_2CO_3 wash but improvements in flux following the second wash were slight. After the first Na_2CO_3 wash, flux levels were essentially constant for the rest of the run and prewash flux for each succeeding wash was about equal to the value following the first wash. Additional washes would not be expected to increase flux as much as the first wash if the fouling constituent removed by the first wash had not reformed before succeeding washes.

Membrane performance after more than 500 hours of operation with NaCl spiked primary sewage and the range of results from special analyses throughout the run are given in Table 15. Product flux at 18 fps was consistently and appreciably less (Fig. 7 and Table 15) than at 31 or 44 fps. Compared to flux from the 44 fps tube, flux at 31 fps was lower before and higher after the first wash.

Run 66; Velocity Effect on Dowex-50 Membranes. Four Dowex-50 X 0.5 membranes preformed on 0.45-μ Acropor supports were tested at feed velocities of 44, 37, 18, and 6.8 fps with feed pressure of 1000 psi. After 1 1/2 hours of operation with 0.01 M NaCl, feed was changed to primary sewage spiked with 0.008 M NaCl. Three hours later, chloride rejections were 72% (Membrane A - 44 fps), 69% (B - 31 fps), 66% (C - 18 fps), and 72% (D - 6.8 fps) at fluxes of 131, 87, 91, and 38 gfd, respectively. Turbidity rejections were all better than 98.5%. At 48 hours, rejections had increased slightly; fluxes had decreased to 106, 65, 70, and 20 gfd.

At 61 hours, the Lucite jacket of Membranes B and D failed and the assembly was removed. Operation was resumed with Membranes A and C (44 and 18 fps). As often observed, the shutdown increased fluxes by ca 30%, but after one day of operation these had decreased to preshutdown levels. The results of a pressure traverse at 85 hours are given in Table 16. The increase in permeability with decreasing pressure is of interest and if confirmed in long-term operation needs to be considered in economic evaluations.

Following the pressure traverse, velocity traverse was made to 10 fps for A and 4.2 fps for C (Table 17). The time at lower velocities (ca 1 1/2 hour) had no effect on rejection or flux for A but flux from C dropped significantly.

TABLE 15

PERFORMANCE OF D-50 X 0.5 MEMBRANES ON 0.45μ PRIMARY SEWAGE (RUN 62)

Feed Velocity fps	Flux gfd	Chloride moles/ℓ	Chloride R_{obs}	Resistance R_{obs}	Turbidity JTU	Turbidity R_{obs}	Org. Carbon mg/ℓ	Org. Carbon R_{obs}	Total Phosphate* moles/ℓ	Total Phosphate* R_{obs}	$Mg^{2+} + Cs^{2+}$ moles/ℓ	$Mg^{2+} + Cs^{2+}$ R_{obs}
Performance after 520 hours operation												
44	74		57	61	0.15	99.6	10	74		70		86
31	87		55	60	0.13	99.7	16	59		73		86
18	37		64	66	0.23	99.5	10	75		77		86
Feed		0.0087			42.0		39		0.0004		0.0014	
Range of Performance Throughout Run												
44					{90 / 99.6		{63 / 88			{68 / 71		{86 / 87
31					{83 / 99.7		{59 / 86			{73 / 76		{79 / 87
18					{95 / 99.6		{70 / 89			{73 / 77		{79 / 87

*325 hours.

TABLE 16

THE EFFECT OF PRESSURE ON PERFORMANCE OF D-50 X 0.5 MEMBRANES ON ACROPOR WITH PRIMARY SEWAGE (RUN 66, 85 HOURS)

Pressure		44 fps			18 fps		
psi	atm	Flux gfd	R_{obs}(Cl) %	Permeability gfd/atm	Flux gfd	R_{obs}(Cl) %	Permeability gfd/atm
1000	68	101	69.6	1.49	61.5	66.4	0.904
750	51	87	65.1	1.70	53.7	61.9	1.05
500	34	72.5	56.8	2.16	43.9	54.3	1.29
750	51	92.7	64.4	1.26	55.6	61.2	1.09
1000	68	107	69.8	1.57	63.4	66.5	0.932

TABLE 17

EFFECT OF CIRCULATION VELOCITY IN SHORT-TERM TRAVERSE WITH DOWEX-50 X 0.5 MEMBRANE (~20 MINUTES AT EACH VELOCITY)

Tube A			Tube C		
Axial Vel. fps	R_{obs}, % (Cl^-)	Flux gfd	Axial Vel. fps	R_{obs}, % (Cl^-)	Flux gfd
44	70	103	18	67	62
30	70	103	12.6	66	62
20	70	105	8.4	65	61
10	68	102	4.2	60	51
30	71	99	12.6	68	47
44	71	100	18	69	53

Operation was continued after the traverses for another 18 hours. Just prior to shutdown at 108 hours rejections were 70% (A) and 66% (C) at fluxes of 93.4 and 50 gfd, respectively. Turbidity rejections were both ca 95%.

At 48 hours, rejection of organic carbon was 70% for Membrane B and 66% for D. Organic carbon rejection of the other membranes varied over the run from 65-80% for A and 63-78% for C.

Run 67; Velocity Effects on Dowex-50 Membranes. Membranes were preformed on 0.45μ Acropor and operated with primary sewage feed (spiked

to 0.008 M NaCl) at velocities of 44, 31, 18 and 13 fps. Membrane performance and run history are shown in Fig. 9.

After 40 hours of operation with primary feed, chloride rejections in order of decreasing feed velocity, were 47%, 49%, 64% and 67% at fluxes of 134, 133, 56 and 45 gfd, respectively. Except for pertubations caused by unscheduled shutdowns, there was a gradual decrease in flux for all membranes for the first 240 hours of the run. By 120 hours run time, the rejections from the membranes operating at 31 and 44 fps were approaching 60%. At 174 hours the jacket of the 13 fps assembly failed and that membrane was removed.

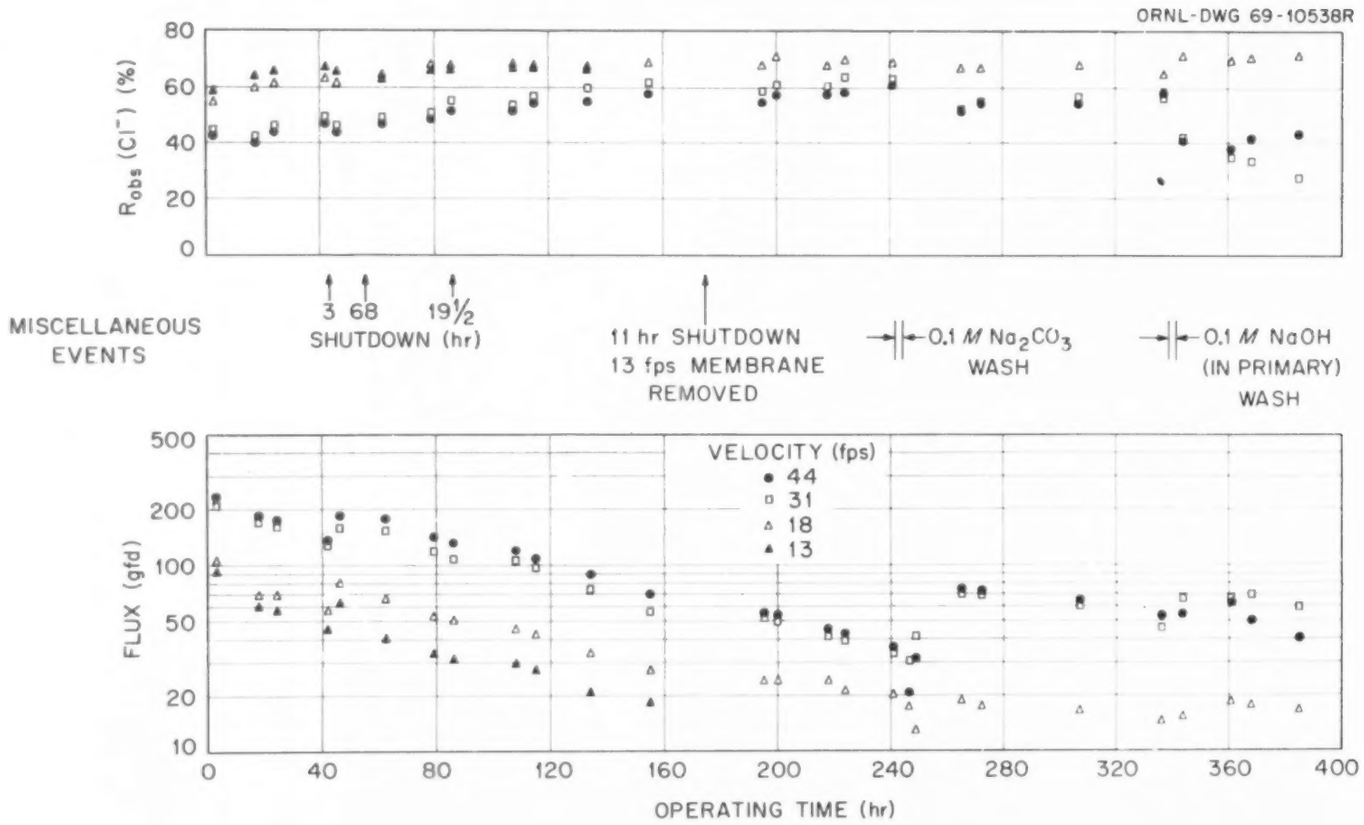
At 241 hours a wash was made with 0.1 M Na_2CO_3. As observed with similar washes in Run 62, fluxes decreased to very low values over the first few hours following the change back to primary sewage, but then increased. Membrane performance before and during the 19 hours following the wash is shown in Table 18. The effect of the wash on flux was (eventually) very large at 44 and 31 fps; however, there was some loss in rejection. The reason for the very limited effect of the wash on the 18 fps membrane is not known.

TABLE 18

MEMBRANE PERFORMANCE BEFORE AND AFTER Na_2CO_3 WASH (RUN 67)

Operating Time hr + min	44 fps		31 fps		18 fps	
	Flux gfd	R_{obs} (Cl) %	Flux gfd	R_{obs} (Cl) %	Flux gfd	R_{obs} (Cl) %
240 + 40	36	62	34	62	20	69
241 + 15 to 246 + 00	Wash with 0.1 M Na_2CO_3					
246 + 13	18		32		14	
247 + 15	24		39		15	
247 + 50	27	59	38	57	18	67
264 + 45	73	53	72	53	19	68
336 + 45	55	51	47	47	15	71

A second rejuvenation was attempted at 339 hours using 0.05 M NaOH in primary sewage. Following the change to primary feed (without base), fluxes increased to nearly the same levels existing 100 hours earlier (following the Na_2CO_3 wash). Unfortunately, these flux increases were accompanied by excessive decreases in rejection. At 19 hours after the change back to primary feed rejections were 34%, 29%, and 68% at fluxes of 66, 68 and 19 gfd. This loss in rejection probably is due to attack by base on some of the seals used; they failed during the next day on the 44 and 31 fps membranes and the run was terminated at 391 hours.



Hyperfiltration of Primary Sewage Effluent
(Run 67, Dowex-50 x 0.5 Membrane on 0.45 μ Acropor Support, 1000 psig, 98°F).

Figure 9

Organic carbon rejections of the membranes running at 44 and 31 fps were ca 62% for the first 41 hours of operation and ranged from 75 to 86% over the latter part of the run. The membranes running at 18 and 13 fps showed organic carbon rejections ranging from 70 to 91%.

Run 68; Fe(III) - PAA Membranes. A polyacrylic acid membrane preformed in the presence of Fe(III) on 0.45μ Acropor was run for evaluation. The use of hydrous Fe(III) oxide as a stabilizer was shown in the OSW program to give a superior PAA membrane. The Dowex-50 membrane, which had been operated at 18 fps in Run 67 for ca 400 hours remained in the circuit. The PAA membrane was run at 44 fps, the Dowex-50 at 18 fps and feed pressure was 1000 psi.

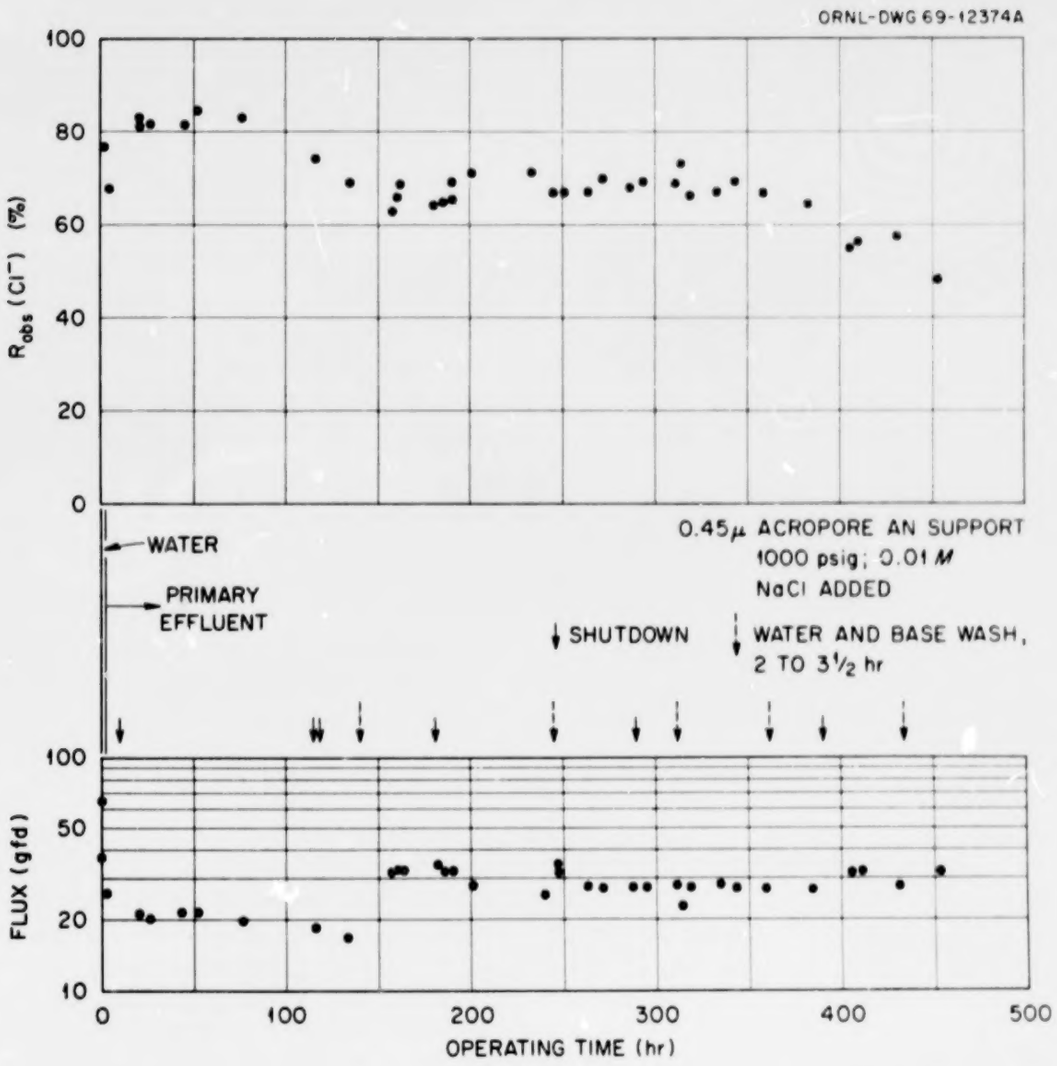
At 25 hours chloride rejections were 49% for the PAA membrane and 69% for the D-50 membrane at fluxes of 93 and 16 gfd, respectively. Though flux through the PAA membrane was still high it was decided to determine the effect of adding NaOH continuously with the salt "spike" solution. Concentrations of the injected solution was set to give a feed concentration of approximately 0.0025 M NaOH and 0.008 M NaCl.

Following the addition of NaOH to the salt supply tank, fluxes through both membranes decreased rapidly. Two hours after the addition, fluxes were 5 gfd for the PAA membrane and 6 gfd for the D-50 membrane. Precipitates obscured the walls of the transparent test section jackets. The concentration of NaOH was raised to 0.005 M at 30 hours. At 77 hours fluxes were 0.5 gfd for the PAA membrane and 0.8 gfd for the D-50 membrane; chloride rejections were ca 50 to 60%.

At 78 hours NaOH addition was stopped. At 94 hours fluxes had increased to 31.4 gfd (PAA) and 3.4 (D-50). Some of the precipitate on the inside of the transparent jacket was removed by this time.

At 96 hours, feed was changed to water and a short 0.1 M NaOH (in water) wash carried out. Water was then used at 0.5 gpm renewal rate to reduce the NaOH concentration before changing back to primary feed. At 102 hours, 2 hours after changing to primary feed, fluxes were 52.7 (PAA) and 4.7 (D-50) gfd. At 114 hours the run was terminated.

Run 69; Fe(III) - PAA Membrane. Figure 10 summarizes results obtained in a 450-hour test in the mobile loop of a poly(acrylic acid) - Fe(III) membrane with primary effluent as feed. The membrane was formed in the corrosion-resistant stationary loop. The support was 0.45μ Acropor AN, mounted in a transparent jacket. Axial velocity was 28 fps. In the formation, 0.05 M NaCl with 5 mg/ℓ iron as $FeCl_3$ was circulated; at pH 6.5 there was essentially no rejection. Fifty mg/ℓ of Acrysol A-5 polyacrylic acid neutralized by NaOH, was added, and R_{obs} (Cl^-) reached 44% at pH 6.7, with flux of 450 gfd at 1000 psi. Acid (HCl) was added to pH 4.2; R_{obs} (Cl^-) was then 52%, flux 290 gfd. After addition of base to pH 7.7, rejection was 82%, and flux dropped to 90 gfd. (A cycle through acid pH values seems usually necessary for stabilization of poly(acrylate) membranes with hydrous oxides). Over the next few days, two more pH



Hyperfiltration Properties of a Polyacrylate Membrane with Primary Effluent Feed.

Figure 10

traverses, encompassing both acidic and basic pH values, were carried out. At pH 6.7, just before transfer to the mobile loop, R_{obs} was 83.5%, and flux, 75 gfd.

Some deterioration of membrane properties occurred during transfer, or as a result of exposure to residual impurities in the mobile loop. With 0.01 M NaCl in water, rejection was 77% and flux 65 gfd (Fig. 10) and there was a further drop before exposure to sewage. Circulation velocity for the run up to 386 hours was probably 18 ft/sec.* On introduction of primary effluent (plus 0.01 M NaCl and no additive), rejection initially decreased, but quickly recovered to over 80%, while flux dropped to 20 gfd. Rejection and flux deteriorated gradually over the next 138 hours.

A pattern of water and alkaline washes (0.1 M NaOH) at intervals of 50 to 100 hours was adopted. The first wash restored flux to about 30 gfd, and flux values scattered around this for the remainder of the run; chloride rejections after the first three washes were 65 to 75%. However, after the fourth wash, rejection began to decline, and by the termination of the run at 450 hours, had fallen to 50%.

Other rejections were measured from time to time during the run: organic carbon, 70 to 95% (the average of eight determinations from feeds containing from 49 to 145 mg/ℓ was 84%); total phosphate, 89%; $Ca^{2+} + Mg^{2+}$, 88%; inorganic carbon, 65 to 80%; and turbidity removals were mostly > 98%.

From the beginning of the run until its failure at 115 hours, a PAA membrane not stabilized by iron (III) was also in the loop. Before exposure to sewage, its rejection of NaCl from 500 ppm in water was 39% with flux of 110 gfd. In contact with sewage, its rejections scattered for the most part between 40 and 50%, and fluxes between 60 and 70 gfd.

Run 70; Dowex-50 and Sephadex Membranes. In Run 70, a "double finger" carried homogenized D-50 membranes on 0.25-μ Millipore (upstream section) and 0.45-μ Acropor support. Another assembly contained a Sephadex C-25 membrane on an 0.45-μ Acropor support. Membranes were preformed in the titanium loop (at X-10) and formation conditions and performance at the end of the formation period are listed in Table 19. Feed pressure was 1000 psi, feed velocity 30.5 fps and (after running for 2 hours with 500 ppm NaCl in city water) the feed was primary sewage continuously spiked to 0.008 M NaCl.

---

*There is some question about the circulation velocity in this run because of uncertainty about the size of the jacket used. The velocity of 18.5 ft/sec seems more consonant with subsequent results with hydrous oxide stabilized PAA membranes.

TABLE 19

MEMBRANE FORMING CONDITIONS AND PERFORMANCE FOR TEST SECTIONS OF RUN 70

	D-50 Membranes		Sephadex
	0.025 μ MP	0.45 μ Acropor	Membrane
Feed Solution	0.01 M NaCl	0.01 M NaCl	0.05 M NaCl
Feed Pressure	1000	1000	1000
Feed pH	9.0	9.0	7.5
Feed Velocity (fps)	22	22	21
Chloride Rejection (%)	83	61	70
Product Flux (gfd)	53	95	210

Performance during the run is shown in Fig. 11 as observed chloride rejection and product flux plotted versus time. At the beginning of the run, with water feed solution, the D-50 membrane on MP (Membrane A) had a flux which was less than 6/10 of that during membrane formation while fluxes of the D-50 membrane on Acropor (Membrane B) and the Sephadex membrane (C) were about twice those at the end of formation. Chloride rejections were considerably below those found at the end of the formation runs, implying that the membranes were damaged in transit.

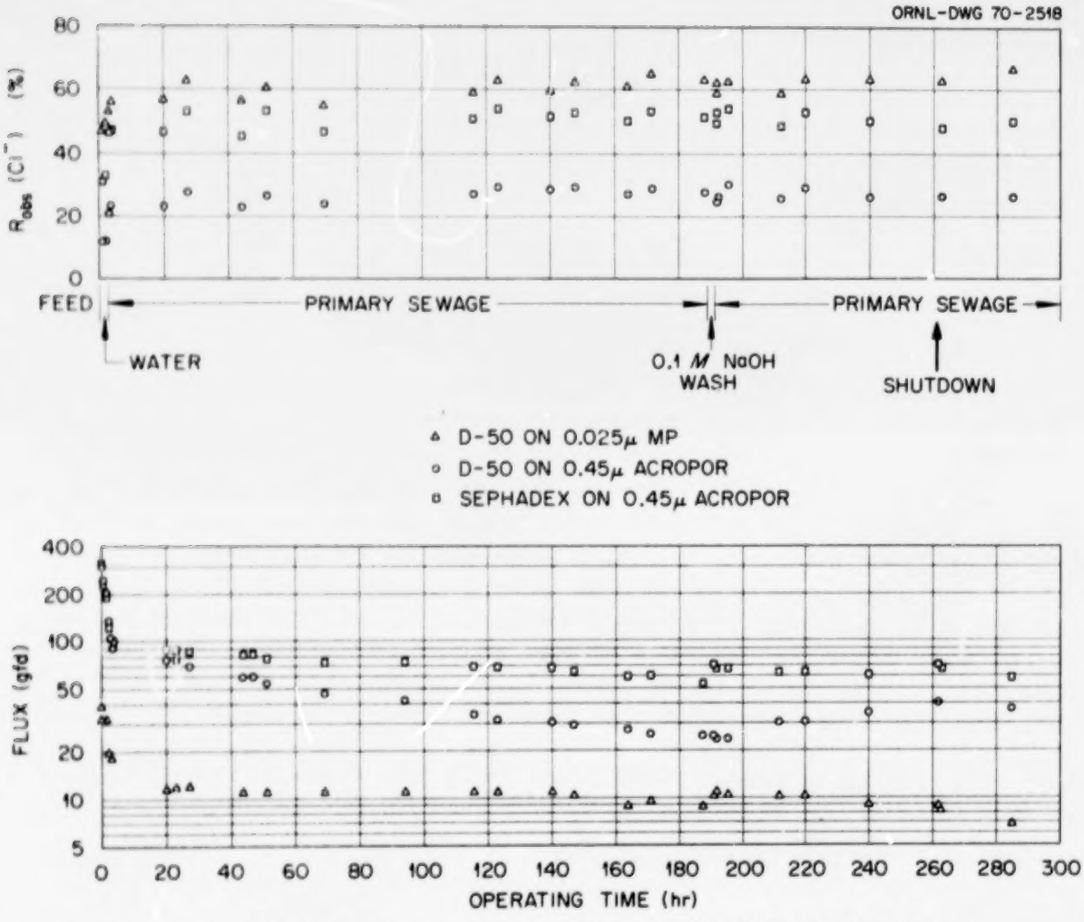
After the change to primary effluent feed, the flux decreased with time was fitted with the relation

$$\Delta \log \text{flux} / \Delta \log \text{time} = b$$

where J = flux, gfd
t = time with sewage feed, hr
b = slope of curve on log J vs. log t coordinates,

Values of b from 0.67 to 32 hours (after the feed change) were −0.142 for Dowex-50 on Acropor and −0.0466 for the Sephadex membranes; and from 32 to 180 hours was −0.566 and −0.195 for Dowex-50 on Acropor and Sephadex, respectively.

After a total, continuous operating time of 188 hours fluxes and Cl^- rejections were 9.1, 25.4, and 54.9 gfd and 63.7%, 27.8% and 52% for Membranes A, B and C, respectively. Feed was then changed to city water for a 1-hour rinse, to a 0.1 M NaOH wash solution for ~1/2 hour and again to city water for a 1-hour rinse. The rinse caused no change in membrane color, but during the wash period Membranes B and C changed from black to dark brown. Membrane A remained white throughout the run.



Run 70: Hyperfiltration of Primary Sewage Effluents with 0.01 *M* NaCl Spike. (Feed Pressure 1000 psig, Feed Velocity 30.5 fps).

Figure 11

The wash resulted in an immediate increase in flux from Membranes A and C followed by a decrease with time. The rest of the run to 285 hours saw the flux and rejection remain the same as their prewash values.

Perhaps the most interesting aspect of this run is the excellent performance of the homogenized Sephadex membrane which maintained essentially constant flux and rejection for well over 200 hours.

Organic carbon rejections ranged from 76 to 92.5% for D-50 Millipore, 72 to 78% for D-50 Acropor and 81 to 92% for the Sephadex-Acropor membrane during this run.

Run 71; Zr(IV)-PAA and Dowex-50 Membranes on Various Supports. Four membranes were tested in Run 71 for an operating period of 222 hours. This run included 3 loop shutdowns, one base wash of the membranes, operation for 169 hours at a feed velocity of 30 fps and 53 hours at 20 fps. After an initial 3-hour operation with city water, the feed was primary sewage spiked with 0.008 M NaCl.

Each membrane was preformed, dynamically, in the titanium loop at X-10. Test section materials and performance at the end of the formation period are listed in Table 20.

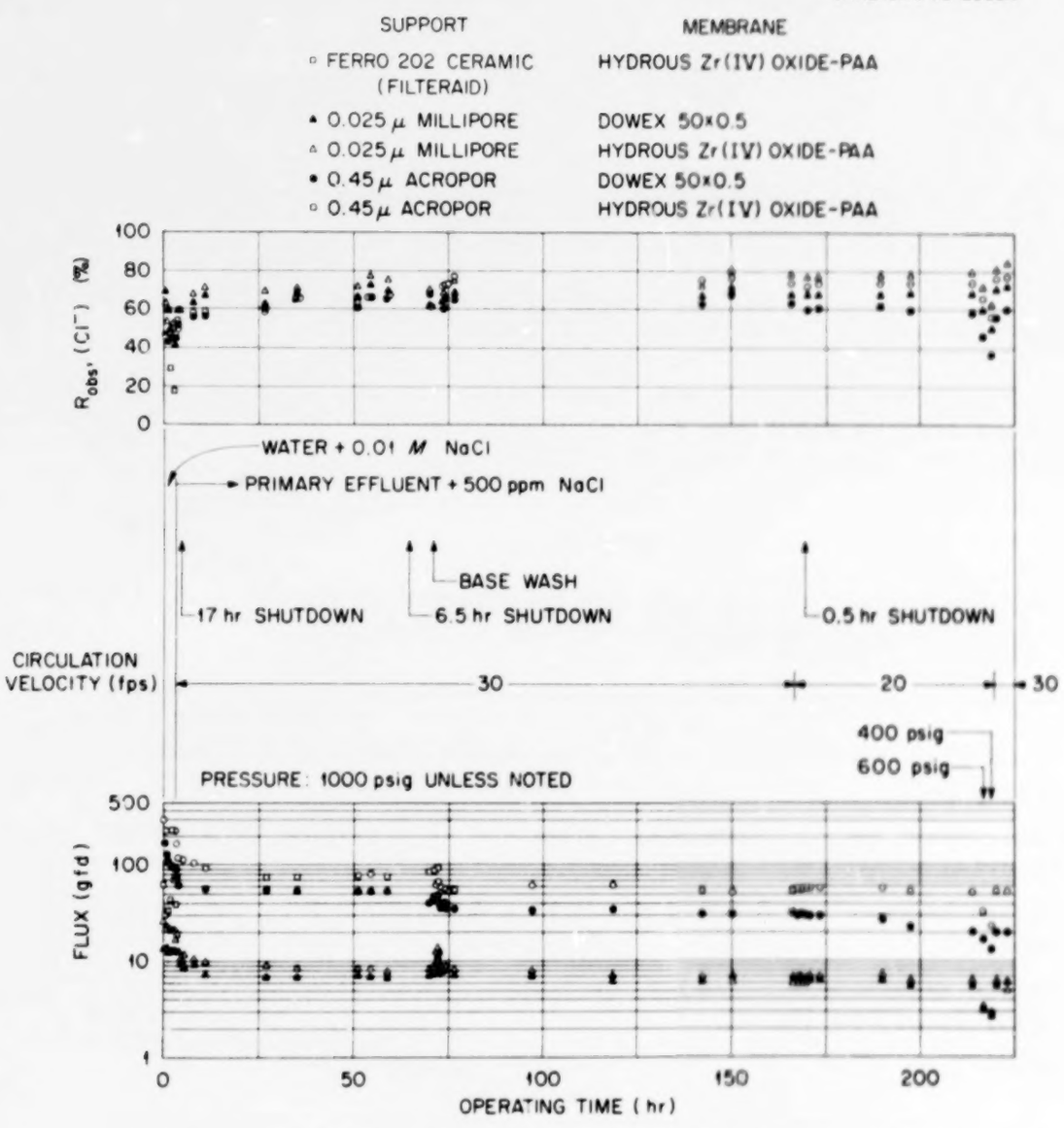
TABLE 20

TEST SECTION MATERIALS AND PERFORMANCE AT END OF MEMBRANE FORMATION FOR RUN 71 MEMBRANES

	B	C	D	E
Molarity NaCl	0.01	0.01	0.05	0.05
Dynamic Membrane Material	Dowex-50	Dowex-50	Zr(IV)+PAA	Zr(IV)+PAA
Membrane Support* Material	0.025 μ M	0.45 μ A	0.025 μ M	0.45 μ A
Chloride Rejection after Formation (%)	83	76	69	74
Product Flux after Formation (gfd)	34	520	35	304

*M = Millipore; A = Acropore

Membrane performance during the run is shown in Fig. 12 as chloride rejection and product flux plotted versus running time.



Hyperfiltration of Effluent from Primary Treatment of Sewage with Dynamically formed Membranes.

Figure 12

When the feed was changed from city water to primary sewage, all membranes had the typical rapid decrease of flux; rejection increased. Performance of the membranes did not seem to be affected by a pressure pulse to 1250 psi or by the 17-hour shutdown which followed.

Flux from the four membranes decreased over a period of about 10 hours following the change to primary sewage, but this was followed by a period (to 68 hours after the feed change) of virtually constant flux from Membranes B and C, a slow decrease with time (of ~7% in 28.5 hours) from Membrane D and a slight increase with time from Membrane E. Chloride rejections were all above 60% during this period.

After a total run time of 71 hours, the loop was rinsed with water, washed with 0.1 M NaOH for 25 minutes and rinsed again. The base wash had little or no effect on the low flux membranes (B and D) and Membranes C and E showed a decrease in flux which did not recover to the prewash levels. Flux from each membrane held relatively constant during the 95-hour period following the base wash and at 167 hours (total run time) feed velocity was reduced to 5 fps in each test section. The reduced velocity caused no significant change in performance of three of the membranes (B, D, and E); but, for Membrane C the rate of flux decline increased and chloride rejection decreased after the velocity change. After running for 6 hours at 20 fps, the membranes were noticeably dirtier and after 47 hours Membrane C appeared to be covered with small black spots.

A pressure traverse from 1000 psi to 400 psi and back at a feed velocity of 20 fps was completed at the end of the run. Results are listed in Table 21.

Analyses for organic carbon rejection were completed periodically during the run and a summary of results is given in Table 22.

Each of the membranes had minimum values of organic carbon rejection at an operating time of 23 hours.

Run 72; Comparison of "Natural" and Sephadex Membranes. The object of this run was to determine the flux-rejection characteristics of a membrane formed from constituents of primary sewage feed (with no additives) on 0.45-μ Acropor support at 1000 psi pressure. For comparison purposes, two preformed Sephadex C-25 membranes were also included in the run. The preformed membranes were prepared in the titanium loop at X-10. The membranes were formed on the top and bottom half of a porous stainless steel tube wrapped with 0.025-μ Millipore and 0.45-μ Acropor, respectively. Preforming conditions and performance at the end of the formation period are listed in Table 23.

Membrane performance during the run is shown in Fig. 13 as chloride rejection and product flux plotted versus the running time. A notable feature of this run was the 214 continuous hours of run time with no shutdowns.

TABLE 21

RUN 71. EFFECT OF PRESSURE ON FLUX AND CHLORIDE REJECTION

Total Run Time (Hr)	Pressure (psig)	Product Flux				Observed Chloride Rejection (%)			
		B	C	D	E	B	C	D	E
214	1000	6.1	20.1	6.2	52.6	65.2	55.0	76.2	70.8
217	600	3.4	17.4	3.4	32.4	56.4	42.5	68.8	62.6
219	400	2.7	13.4	2.8	23.8	46.5	33.8	59.6	53.1
220	1000	6.1	20.1	6.2	50.4	67.2	52.6	77.9	72.8

TABLE 22

RUN 71. SUMMARY OF ORGANIC CARBON REJECTION RESULTS

	Observed Organic Carbon Rejection (%)			
	B	C	D	E
Approximate Time Average	83	81	87	93
Range During Run	74-90	67-85	71-94	75-94

TABLE 23

TEST SECTION MATERIALS AND PERFORMANCE AT END OF FORMATION FOR RUN 72 MEMBRANES (FEED: 0.01 M NaCl)

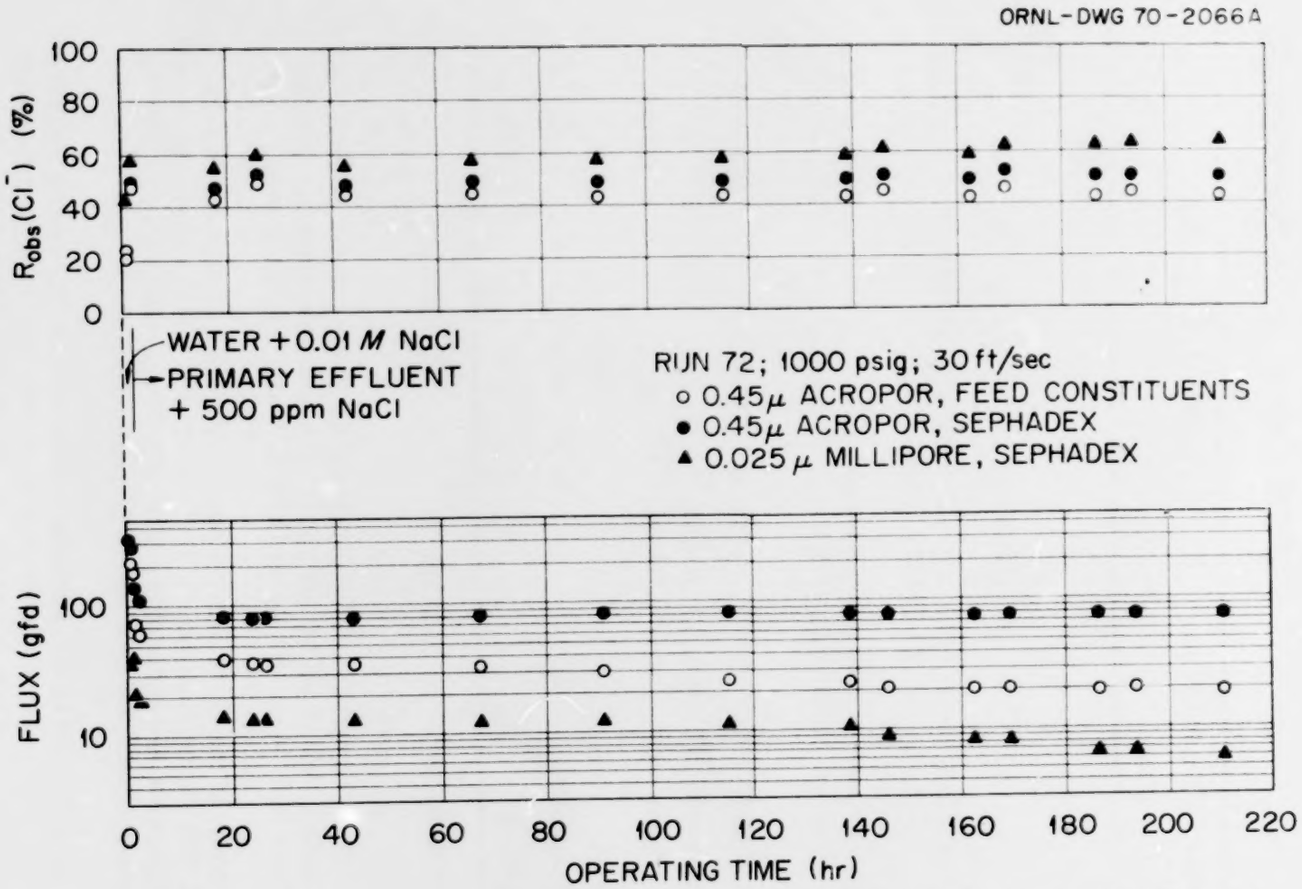
Dynamic Membrane Material	None	Sephadex C-25 + Filter Aid	Sephadex C-25 + Filter Aid
Membrane Support Material*	0.45μ A	0.025μ M	0.45μ A
Axial Velocity, ft/sec	30	33	33
Pressure, psig	1000	1000	1000
Feed, pH	–	8.0	8.0
Chloride Rejection, (%)	–	80%	57%
Flux, (gfd)	–	78	594

*A = Acropor; M = Millipore

The run was started with spiked city water feed (~0.01 M NaCl) at 1000 psi and an axial velocity of 30 fps. One and one quarter hours after startup, feed was switched to spiked primary sewage feed.

Within one hour after switching from city water feed to primary sewage, the flux had decreased to 35 to 45% of its city-water value and rejection had increased significantly for all three membranes. Within two hours the sewage-membrane reached 47% rejection at 61 gfd flux.

Rejection was substantially constant from 18 to 210 hours running time. The Sephadex membrane on 0.45μ Acropor had superior performance and only a modest flux decline (from 83 to 74 gfd) during this time. The untreated 0.45μ Acropor flux declined from 39 to 19 gfd and the Sephadex on 0.025μ Millipore flux declined from 14 to 6 gfd during the last 192 hours.



Comparison of Hyperfiltration of Primary Sewage Effluent by Membrane Formed from Feed Constituents with Sephadex CM C-50 Membranes.

Figure 13

Organic carbon rejection of all membranes ranged between 75 and 93% during the run. Organic carbon content of the feed was 46-85 ppm, but there was no apparent correlation between rejection and feed concentration.

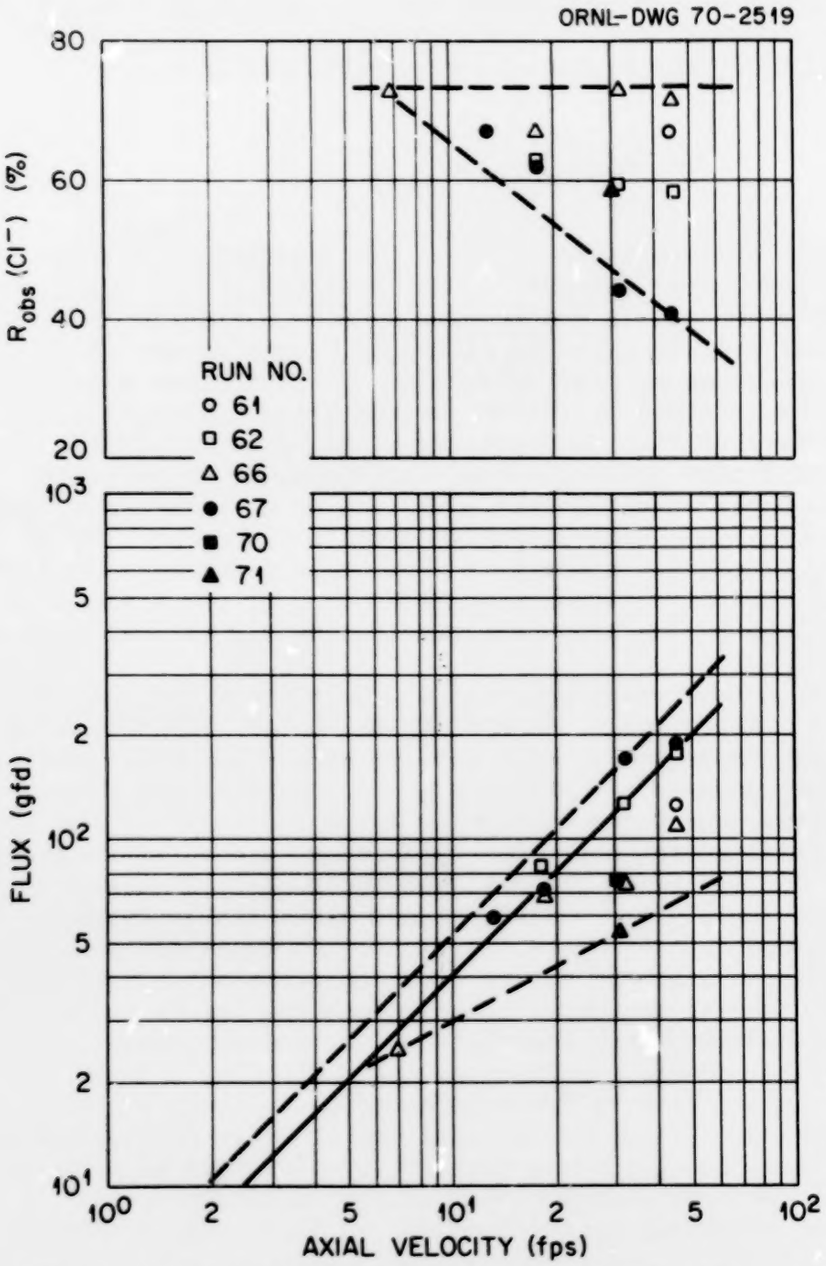
DISCUSSION

Significance of results obtained in the preliminary survey and long-term runs have been outlined in the Summary section. Pressure effects have been treated in the Results section. Briefly, rejection with sewage feeds depends strongly on pressure, and it may be necessary to operate at pressures as high as 1000 psi for salt removals of 60%. Unfortunately, in extended operation, permeability (flux/pressure) appears to become less at higher pressures, and production rate is not increased to the extent one might hope with increase in pressure. However, fluxes appear high enough (50-70 gfd as compared to 10 to 20 gfd currently obtainable with cellulose acetate membranes) for the method to be of practical interest if flux decline can be slowed sufficiently without excessive circulation velocity. We shall expand here on the implications of the long term runs for this question.

But, first, a few words regarding the relatively frequent shutdowns may be in order. While the ability of most of the membranes to survive these interruptions without serious effect on performance is encouraging, the occurrences, at least those not resulting from power failures, may raise questions concerning the suitability of the technique for practical operations. Our experience is not pertinent to this subject. Our equipment was designed to simulate in small-scale operation a wide variety of conditions, and bears little relation to the design applicable to an operating plant. It contained a variety of safety devices, which were set to cause complete shutdowns when operating conditions varied significantly from the preset values. Some stoppages came about from our inexperience in handling sewage, such as cleaning of intake screens too infrequently. Finally, a large fraction of stoppages resulted from failures in experimental test sections. For example, failures of transparent jackets and of seals for the porous sheets used as membrane supports, both of which we were developing during the period. We have overcome many of our difficulties with these, and in any case, practical porous supports would be very different.

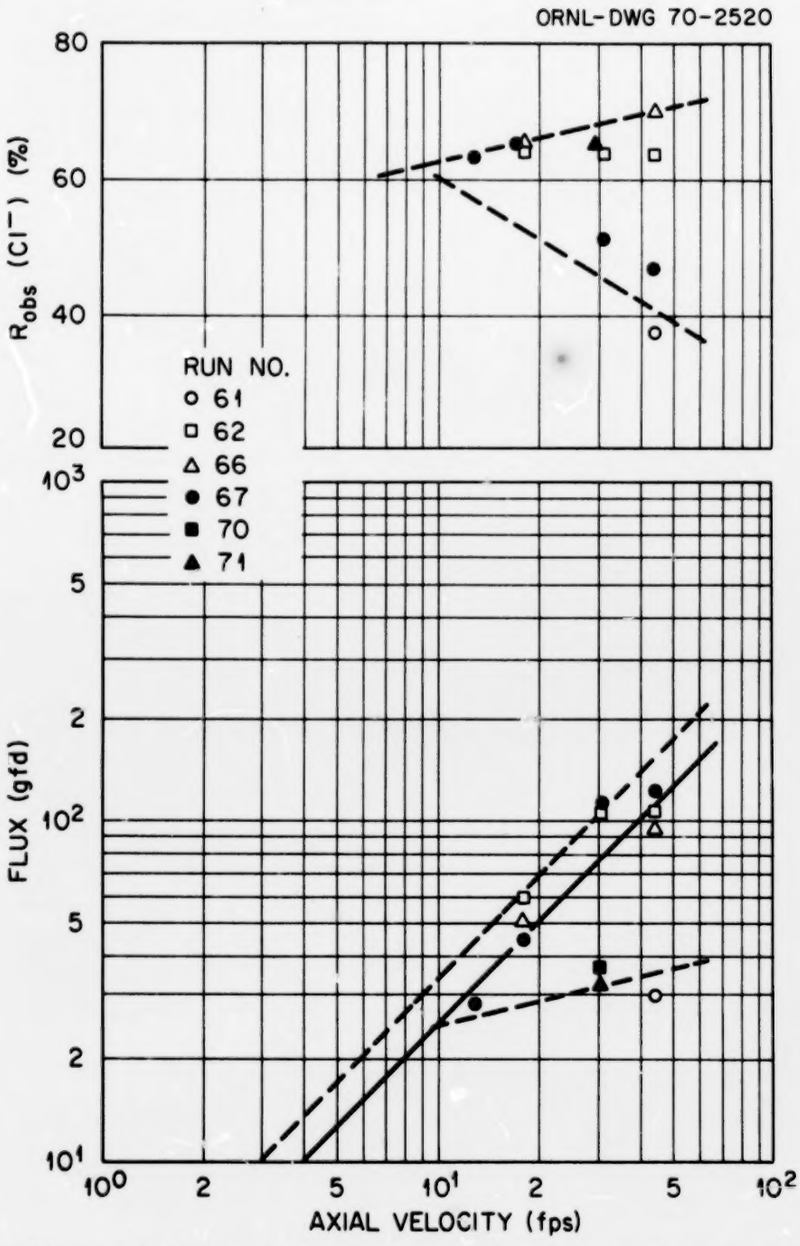
Velocity Effects

A substantial number of runs were made with Dowex-50 preformed membranes with 0.45-μ Acropor supports at 1000 psig and various velocities (Table 4). The effect of axial velocity on flux and rejection at 20, 100, 200 and 400 hours forthese tests is shown in Figs. 14 through 17. On these plots the dotted lines are drawn to include the bulk of the points and thus provide an estimate of the uncontrolled variation in the tests, the solid line is the "best fit" to the data points.



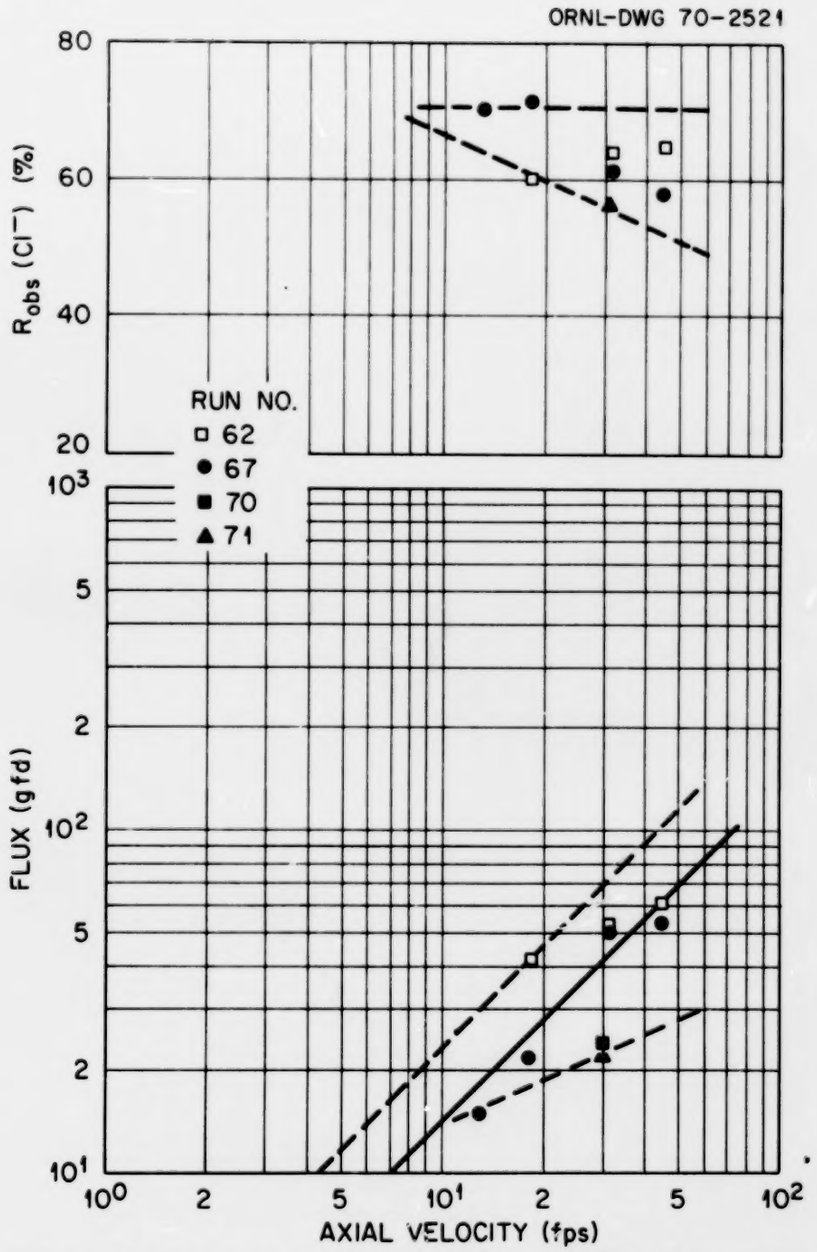
Effect of Axial Velocity on Flux and Rejection of Preformed Dowex 50 x 0.25 Membrane After 20 hr of Operation with Primary Sewage Feed (1000 psig 0.45μ Acropor Support).

Figure 14



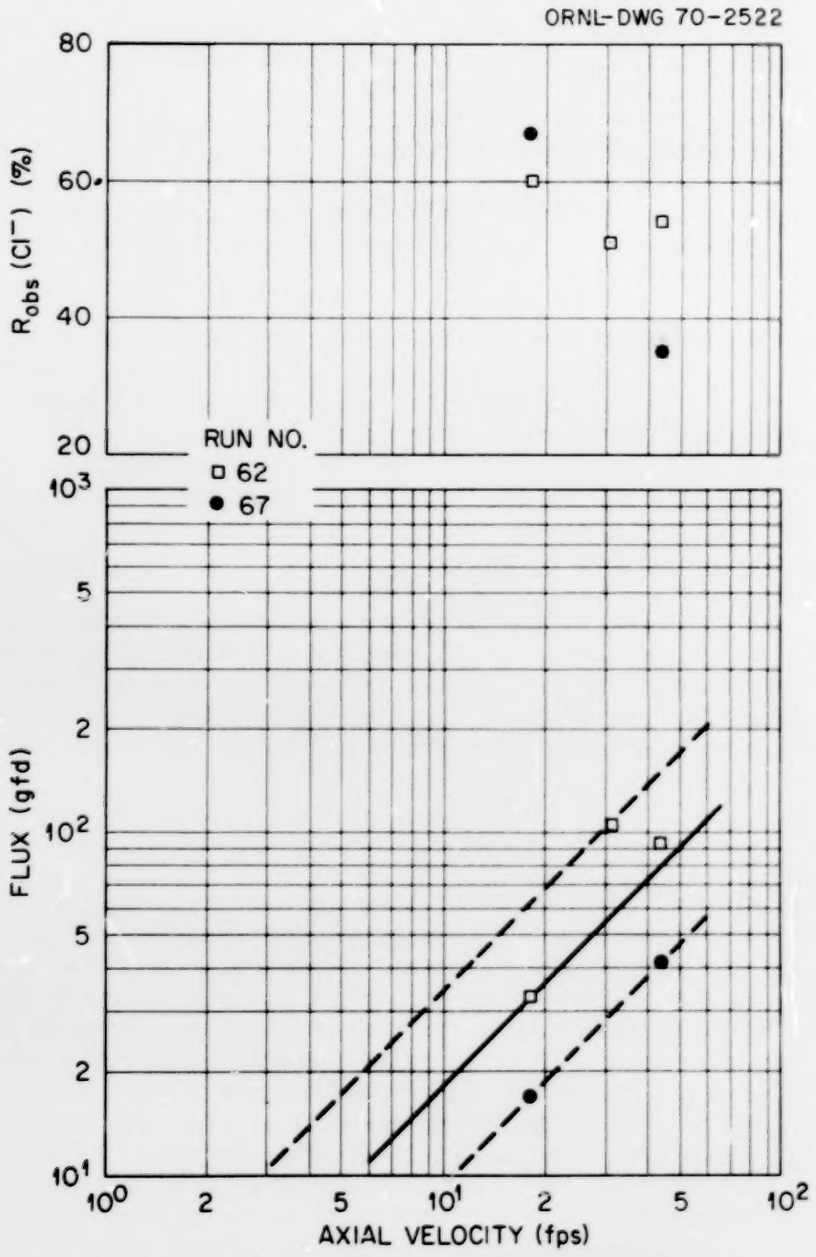
Effect of Axial Velocity on Flux and Rejection of Preformed Dowex 50 x 0.25 Membrane After 100 hr of Operation with Primary Sewage Feed (1000 psig 0.45 μ Acropor Support.

Figure 15



Effect of Axial Velocity on Flux and Rejection of Preformed Dowex 50 x 0.25 Membrane After 200hr of Operation with Primary Sewage Feed (1000psig 0.45 μ Acropor Support).

Figure 16



Effect of Axial Velocity on Flux and Rejection of Preformed Dowex 50 x 0.25 Membrane After 400 hr of Operation with Primary Sewage Feed (1000 psig 0.45 μ Acropor Support).

Figure 17

The dotted lines from Figs. 14 and 15 are shown as solid lines on Figs. 18 and 19 together with the results from other membranes tested at the trailer loop.

The following observations seem notable:

1. Maximum (and probably "best fit") flux seems proportional to axial velocity. Minimum flux is more nearly proportional to square root of velocity.

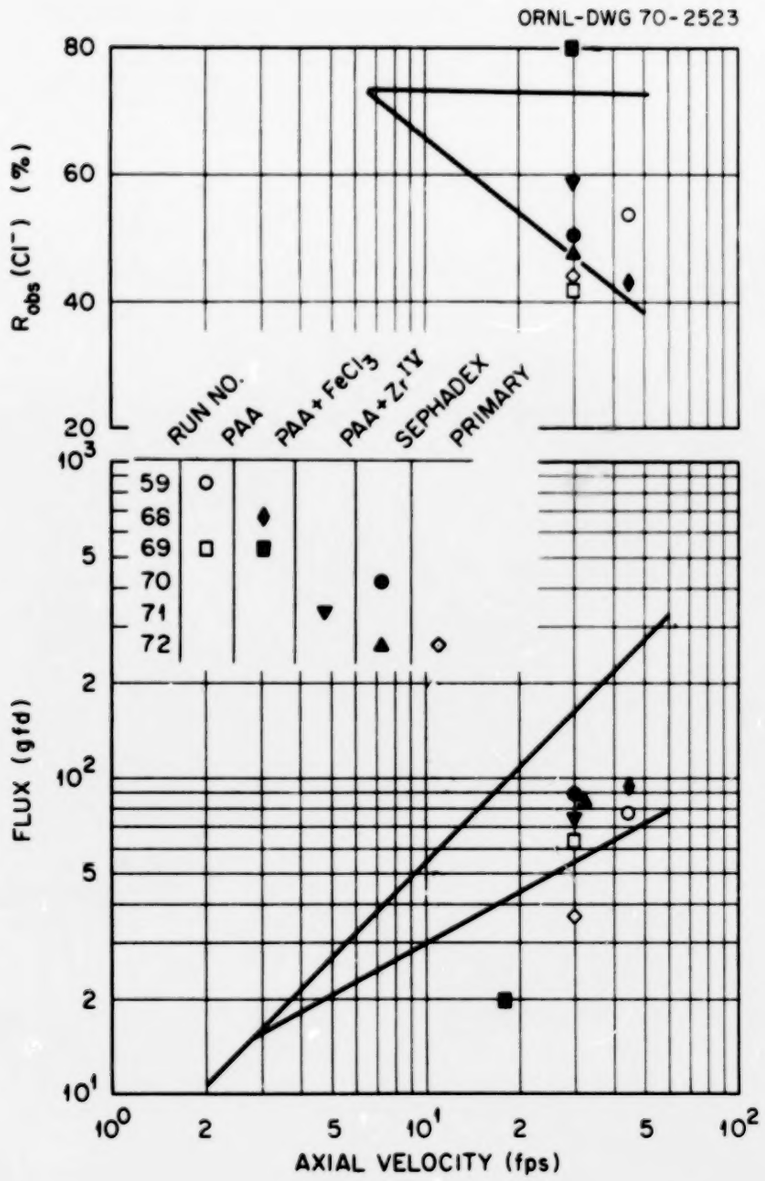
2. The greatest range of variation in observed rejection with Dowex-50 membranes was observed at the highest axial velocity. Whether this is because fewer tests (and hence inadequate statistics) were made at low velocities or whether some membranes are too fragile to be run at high velocities cannot be determined from the present results. It is notable that in Runs 62 and 66 the rejections were above ~60% and essentially independent of velocity while in Run 67 the highest rejection was observed at the lowest velocity.

3. The bulk of the results for different membrane materials fell within the scatter band for the Dowex-50 results. The grouping of points within the band limits was somewhat better (i.e., less scatter) for the 100-hour results than for the 20-hour results, indicating that possible differences in membrane chemistry were minimized after 100 hours exposure to primary sewage.

Flux Decline

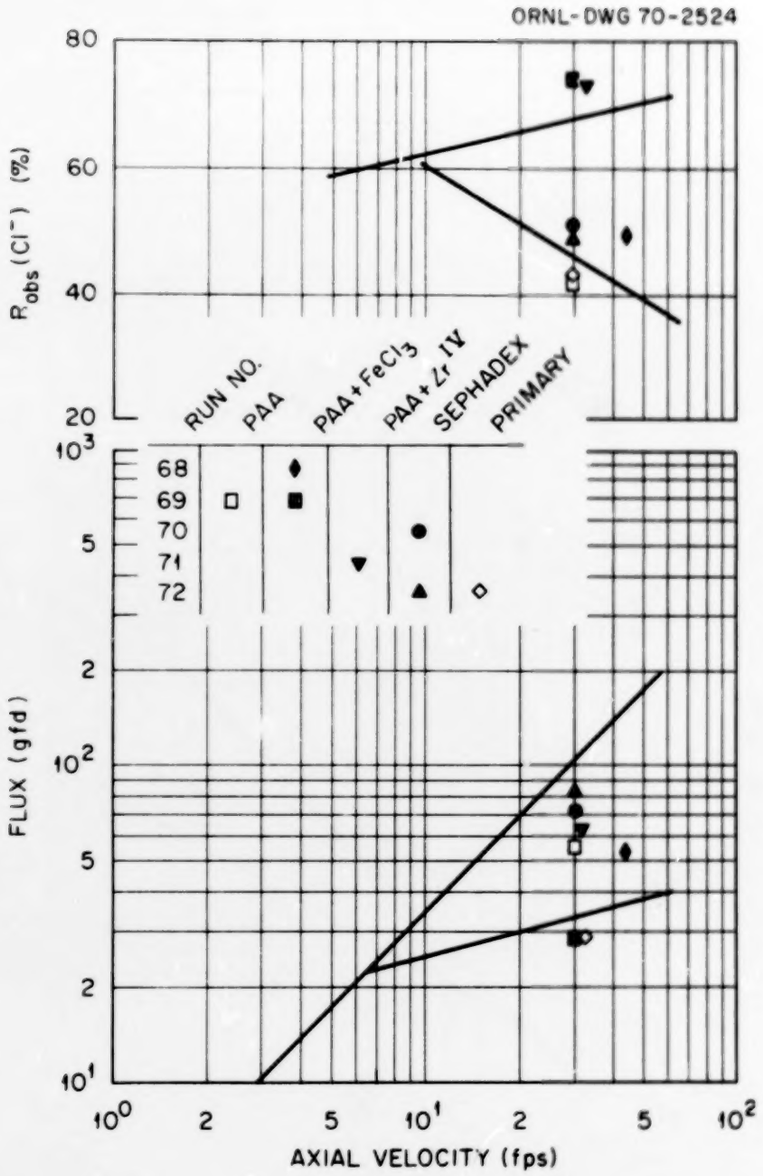
Evaluation of flux as a function of time is difficult because of the many unscheduled shutdowns as well as scheduled changes in operating conditions required for diagnostic purposes. However, Run 72 was operated for 210 hours with no shutdowns and no scheduled changes in operating conditions. Flux declines were modest in this test, i.e., from 80 to 76.6 gfd from 20 to 210 hours with a Sephadex membrane on 0.45-μ Acropor support at 30 ft/sec axial velocity. The results gave a good straight line on a plot of log flux vs time. When plotted as log flux vs log time the slope for this period was approximately −0.04. No data for cellulose acetate membranes operating at these high fluxes are known to us. However, limited data available (1-3) indicate that serious flux decline occurs with cellulose acetate membranes exposed to sewage under conventional operating conditions when the initial flux is 10 to 20 gfd. Only by chemical cleaning of membranes (6) or dropping the flux to ~2 gfd (2) can flux decline effects be minimized.

Based on the results from plots of flux as a function of velocity (Figs. 14 to 17) flux decline as a function of time for the Dowex-50 results at 20 ft/sec is shown in Fig. 20 on both semi-log and log-log plots. These plots include the estimate of the best line through the points as well as the maximum and minimum values obtained from Figs. 14 to 17.



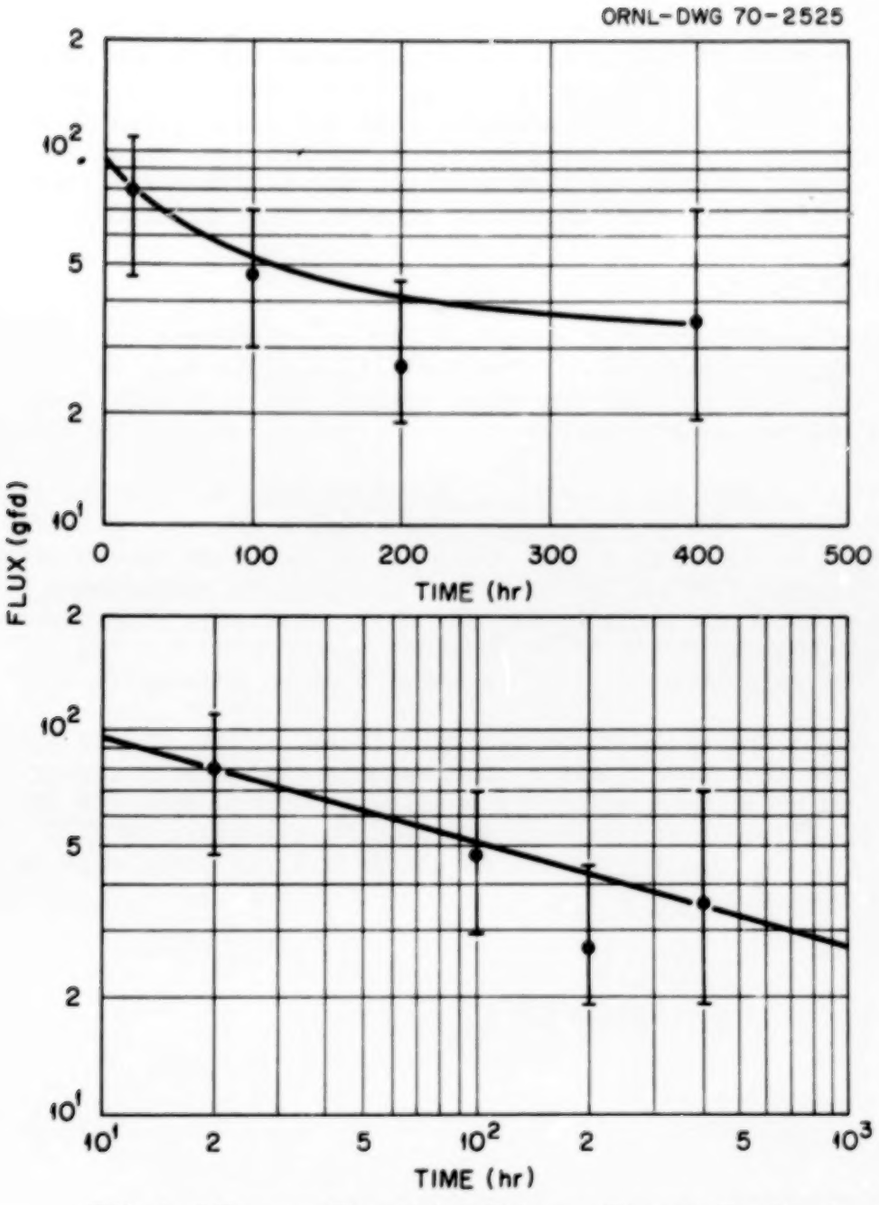
Comparison of Different Membranes and Primary Sewage Alone with Performance of Dowex 50x 0.25 Membrane (Solid Curves Outline Scatter Band of Dowex 50 from Figure 14) after 20 hr Operation with Primary Sewage (1000 psig, 0.45μ Acropor Support).

Figure 18



Comparison of Different Membranes and Primary Sewage Alone with Performance of Dowex 50x0.25 Membrane (Solid Curves Outline Scatter Band of Dowex 50 from Figure 15) after 100 hr Operation with Primary Sewage (1000 psig, 0.45μ Acropor Support).

Figure 19



Effect of Time on Flux Using Primary Sewage Feed and Preformed Dowex 50 x 0.25 Membrane at an Axial Velocity of 20 fps. (1000 psig, 0.45 μ Acropor Support, Points and Limits on Curves are best fit, Maximum and Minimum Values from Figures 14-17).

Figure 20

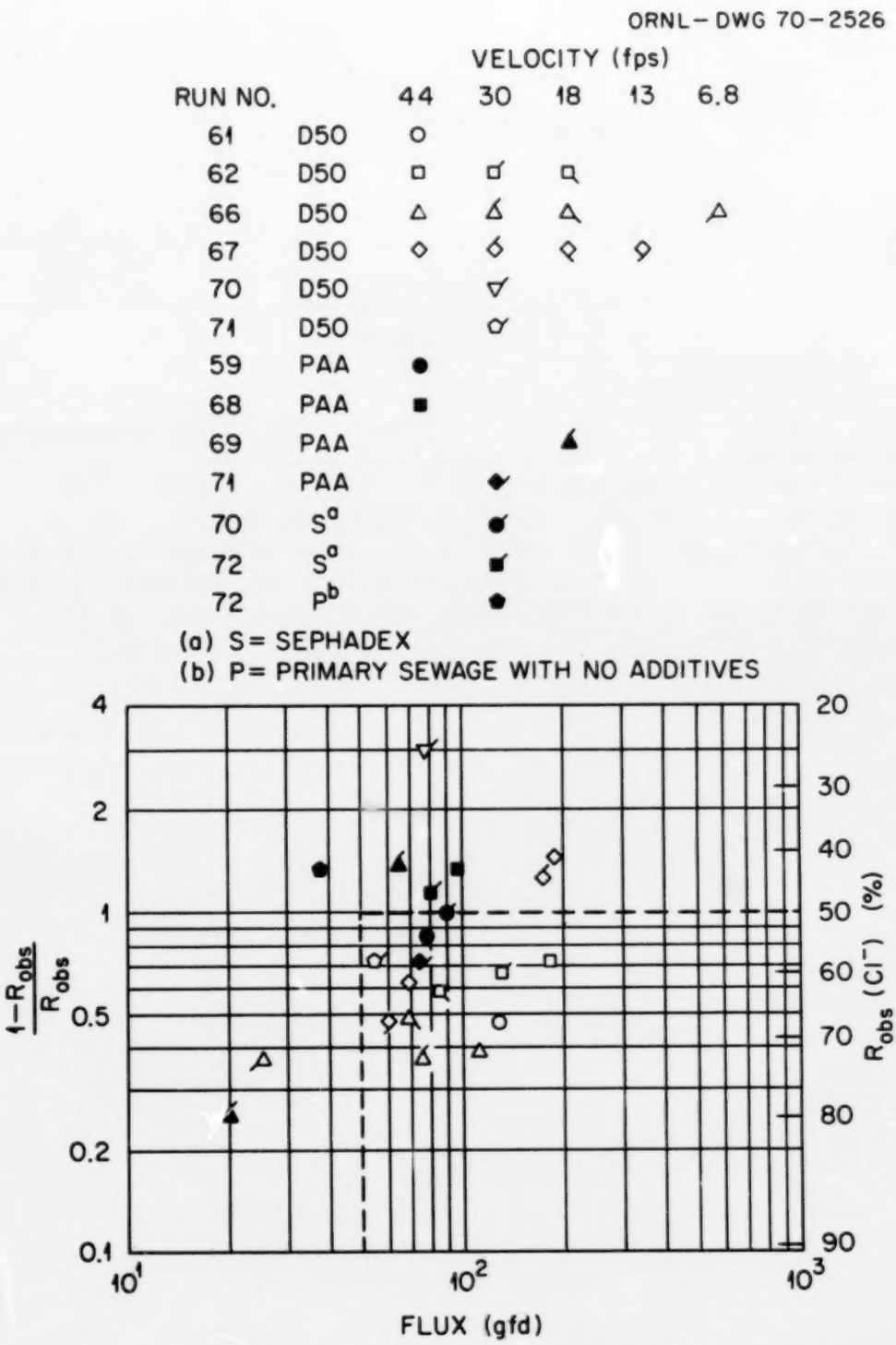
The straight line on the log-log plot has a slope of −0.27. The results shown on Fig. 20 should not be extrapolated beyond 400 hours because in many runs flux decline was arrested by base washes, accidental shutdowns, etc. It seems probable that the flux observed after 200 to 400 hours running time could be maintained at that value for substantially longer periods of time provided the membrane is given a periodic base wash, pressure excursion or some other treatment.

Rejection-Flux Relation

The performance of dynamic membranes can be summarized on a plot of $(1 - R_{obs})/R_{obs}$ vs the flux J. The ratio $(1 - R_{obs})/R_{obs}$ was chosen instead of simply R_{obs} because the ratio expands the rejection scale for both high and low rejections.

Figure 21 is a plot of $[(1 - R_{obs})/R_{obs}]$ vs flux for trailer runs using primary sewage effluent as feed. The results are for 20 hours exposure to the sewage feed, a time which was selected as representing a compromise between showing the effect of the feed on performance and still retaining chemical characteristics of the membrane. The dashed line encloses a desirable set of performance characteristics i.e., greater than 50% rejection at fluxes greater than 50 gallons/ft^2.

Considering all membranes and all velocities, almost 60% of the tests were in the favorable region. Eliminating the primary sewage (no membrane) point and the point for a velocity of 6.8 fps, 67% of the tests with all membranes were in the favorable region; of the Dowex-50 tests along (neglecting the result at 6.8 fps), 77% were in the favorable region.



Flux — Rejection Results after 20 hr Exposure to Primary Sewage Effluent at 1000 psig Operating Pressure.

Figure 21

ACKNOWLEDGMENTS

This work was carried out by J. A. Dahlheimer, J. S. Johnson, W. R. Mixon, and K. A. Kraus. J. R. Love assisted in operation of the loop.

We thank Jesse M. Cohen and Warren A. Schwartz of the Cincinnati Water Research Laboratory, Federal Water Pollution Control Administration, for their encouragement in this work and their advice in a field unfamiliar to us. We have received extremely helpful cooperation from the City of Oak Ridge, particularly from Thomas C. Stephens, supervisor of the Municipal Sewage Plants and O. K. Rickman, Director of Public Works. Others helpful in this work include A. J. Shor, who contributed to the design of the Mobile Unit and J. R. Hart, who supervised its assembly; W. G. Sisson, who suggested the design of the test section with transparent pressure jackets; C. G. Westmoreland, J. Csurny, Neva Harrison, C. G. West, as well as Hart and Sisson, for technical assistance; J. N. Baird and D. C. Michelson, who worked out analytical procedures.

REFERENCES

1. "Summary Report, The Advanced Waste Treatment Research Program, January 1962 through June 1964, "AWTR-14, Public Health Service Publication No. 999-WP-24.

2. Merten, Ulrich and Bray, D. T., Proc. 3rd International Conference on Water Pollution Research (Munich, Germany), 3: 315 (1966).

3. Suddak, R. G. and Nusbaum, I., "Pilot Plant Operation of Spiral Wound Reverse Osmosis Systems," Gulf General Atomic Report GA-8515 (1968).

4. Hindin, Ervin, Bennett, P. J., and Narayanan, S. S., Water and Sewage Works, 116: 466 (1969).

5. Hauck, A. R., and Sourirajan, S., Environmental Science & Technology, 3: 1269 (1969).

6. Bregman, J. I., Environmental Science & Technology, 4: 296 (1970).

7. Kraus, K. A., Shor, A. J. and Johnson, J. S., Desalination, 2: 243 (1967).

8. Perona, J. J., Butt, F. H., Fleming, S. M., Mayr, S. T., Spitz, R. A., Brown, M. K., Cochran, H. D., Kraus, K. A. and Johnson, J. S., Environmental Science & Technology, 1: 391 (1967).

9. Savage, H. C., Bolton, N. E., Phillips, H. O., Kraus, K. A., and Johnson, J. S., Water and Sewage Works, 116: 192 (1969).

10. Shor, A. J., Kraus, K. A., Johnson, J. S. and Smith, W. T., Jr., Ind. Eng. Chem. Fundamentals, 7: 44 (1968).

11. Baldwin, W. H., Holcomb, D. L. and Johnson, J. S., J. Polymer Sci., 3, Part A, 833 (1965).

12. Sheppard, J. D. and Thomas, D. G., Appl. Polymer Symposia, No. 13, p. 121, A. F. Turbak, Ed., John Wiley & Sons (1970).

13. Dahlheimer, J. A., Thomas, D. G. and Kraus, K. A., Eng. Chem. Process Design and Dev., 9(4) (1970).

14. Johnson, J. S., Jr., Kraus, K. A., Fleming, S. M., Cochran, H. D., Jr. and Perona, J. J., Desalination, 5: 359 (1968).

15. Standard Methods for the Examination of Water and Wastewater, 12th Ed., American Public Health Association, Washington, D. C. (1965) p. 236.

16. Johnson, J. S., Dresner, L. and Kraus, K. A., "Hyperfiltration (Reverse Osmosis)", Chapter 8 of Principles of Desalination, Academic Press (New York) April 1966.

* U. S. GOVERNMENT PRINTING OFFICE : 1970 O - 411-033

RECEIVED
NATIONAL TECHNICAL
INFORMATION SERVICE
MAR 8 1971

As the Nation's principal conservation agency, the Department of the Interior has basic responsibilities for water, fish, wildlife, mineral, land, park, and recreational resources. Indian and Territorial affairs are other major concerns of America's "Department of Natural Resources."

The Department works to assure the wisest choice in managing all our resources so each will make its full contribution to a better United States—now and in the future.